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The Impact of Nutrient Availability and Algal Community on Carbon Isotope Fractionaion in Crystal Lake, Clark County, Ohio

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THE IMPACT OF NUTRIENT AVAILABILITY AND ALGAL COMMUNITY ON CARBON ISOTOPE FRACTIONATION IN CRYSTAL LAKE, CLARK COUNTY, OHIO

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY April R. Wisebaker ENTITLED The Affect of Nutrient Availability and Algal Community on Carbon Isotope Fractionation in Crystal Lake, Clark County, Ohio BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS OF THE DEGREE OF MASTERS OF SCIENCE.

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Abstract

Wisebaker, April R. M.S., Department of Earth and Environmental Sciences, Wright State University, 2008. The impact of nutrient availability and algal community on carbon isotope fractionation in Crystal Lakes, Clark County, Ohio.

Crystal Lakes are a group of four interconnected lakes, located in southwestern Clark County, Ohio. Several studies have looked at separate geochemical and isotopic information at this location. However, no one has thoroughly studied the relationship between the algal community, geochemistry, and carbon isotope fractionation within Crystal Lake. The fractionation of carbon isotopes of dissolved inorganic carbonate is greatly affected by the process of photosynthesis; the amount of photosynthesis is affected by the amount of algae in the aquatic community; the amount of algae is affected by the available nutrients in system. Therefore, there should be a correlation between the nutrients in the water column, the amount of algae, and the extent of carbon isotope fractionation. If such a correlation is found, it could be used as a proxy for paleonutrient availability.

To determine this correlation, water samples were collected via submersible pump every 1.5 meters at approximately the deepest location in Crystal Lake. Several parameters that are important indicators of photosynthesis, such as dissolved oxygen and pH, were measured in situ. The collected samples were analyzed for nutrient and chlorophyll content; samples were also sent out for carbon isotope analysis.

The measured values of $\delta^{13}C$ in Crystal Lake are highest in areas of photosynthesis, and decrease in the hypolimnion where decomposition of accumulated biomass occurs. There is a clear trend between carbon isotope fractionation and photosynthetic indicators, such as dissolved oxygen and pH. Trends between several nutrient concentrations and fractionation was also observed. Samples with $\delta^{13}C$ values less than -10 ‰ V-PDB have pH values below 8 and little dissolved oxygen (0-1 mg/L).

Samples with $\delta^{13}C$ values between -9 and -6 ‰ V-PDB have pH values greater than 8, dissolved oxygen levels between 5-20 mg/L, silica concentrations below 3.25 mg/L, magnesium concentrations below 27 ppm, and calcium concentrations above 60 mg/L. Samples with $\delta^{13}C$ values above -6 ‰ V-PDB have a pH between 8-9, dissolved oxygen levels between 10-30 mg/L, silica concentrations above 3.25 mg/L, magnesium concentrations above 27 ppm, and calcium concentrations below 60 mg/L. More research is needed to corroborate these trends and expand our understanding of the affect of nutrient concentrations on carbon isotope fractionation.

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1.0 Introduction

1.1 Carbon isotopes, nutrients, and photosynthesis

The process of photosynthesis requires several factors, namely carbon dioxide, water, light, and nutrients. In an aqueous environment, the most common limiting factor of photosynthesis is the nutrient content. The amount of photosynthesis, therefore, depends on the nutrient availability.

Isotope analysis in limnological studies can reveal new insights into complex biogeochemical interactions within aqueous environments. The most common isotopes studied in such environments are those of carbon. Changes in the ratios of the two stable carbon isotopes, ^{12}C and ^{13}C, are referred to as the fractionation of these isotopes (Clark & Fritz, 1997). In an aqueous environment, photosynthesis is the one of the most important processes that causes fractionation of carbon isotopes (Bade, 2006).

When algae photosynthesize, most preferentially consume the lighter ^{12}C isotope, leaving their surrounding environment enriched in ^{13}C, and changing the carbon isotope ratio in the water (Bade et al., 2006). The extent of carbon isotope fractionation in the aqueous environment depends on several factors. These include the species of algae, the abundance of algae (Bade et al., 2006), the amount of carbonate precipitation and dissolution, and the ^{13}C of atmospheric CO_2 (Clark & Fritz, 1997). The types and amounts of algae are also dependent on nutrient availability, the amount of light penetration (Sigee, 2005), and the season (Wetzel, 2001). Since nutrient availability is a major factor that influences the extent of photosynthesis, and that the amount of photosynthesis that occurs is dependent on the amounts and types of algae and other photosynthetic phytoplankton within the water column, one would expect that the residual ^{13}C in the water column would reflect nutrient availability. The greater the nutrients, the more photosynthesis occurs, and the greater the amount of carbon isotope

fractionation. However, varying seasons affect the amount of nutrients available for algae. Different seasons also cause differences in algal communities. Also, different types of algae may fractionate carbon isotopes differently. Therefore, it is difficult to compute the $\delta^{13}C$-nutrient relationship.

1.2 Purpose of this Study

By studying the nutrient content, the types and amount of algae, and the fractionation of carbon over seasons, we may be able to find a specific correlation, which could then be used to create a model to interpret other limnological and paleolimnological data. These new insights may be useful in future paleoclimatological studies. The purpose of this study is to identify each of these factors and the processes controlling them. If we can correlate the extent of carbon isotope fractionation to various algal communities, we may be able to use this as a proxy for paleonutrient availability and past productivity.

2.0 Background Information

2.1 Study Site

2.1.1 Physical description

Crystal Lake is a series of four small, interconnected lakes (North Lake, South Lake, Hidden Lake, and Main Lake) located in southwestern Clark County in Ohio (Fig. 1). The surface area of Crystal Lake (Main Lake), excluding an island located in the lake, is about 12.5 acres (Cheng, personal communication), with a maximum depth of 11.6 meters (Woodruff, 1999) and a mean depth of about 6 meters (Talsna & Lazorchak, 1975). The main lake of Crystal Lake, where this study focused on, is about 12.5 acres. Crystal Lake has a volume of about 53 million gallons (Cheng, personal communication). The bedrock of Crystal Lake is Ordovician dolomitic limestone with interbeds of calcareous shales (Woodruff, 1999). The soil around the area is peat-like, and part of the Mad River aquifer (Talsna & Lazorchak, 1975). Crystal Lake is underlain by glacial outwash deposits to about 75 m (Norris et al., 1952).

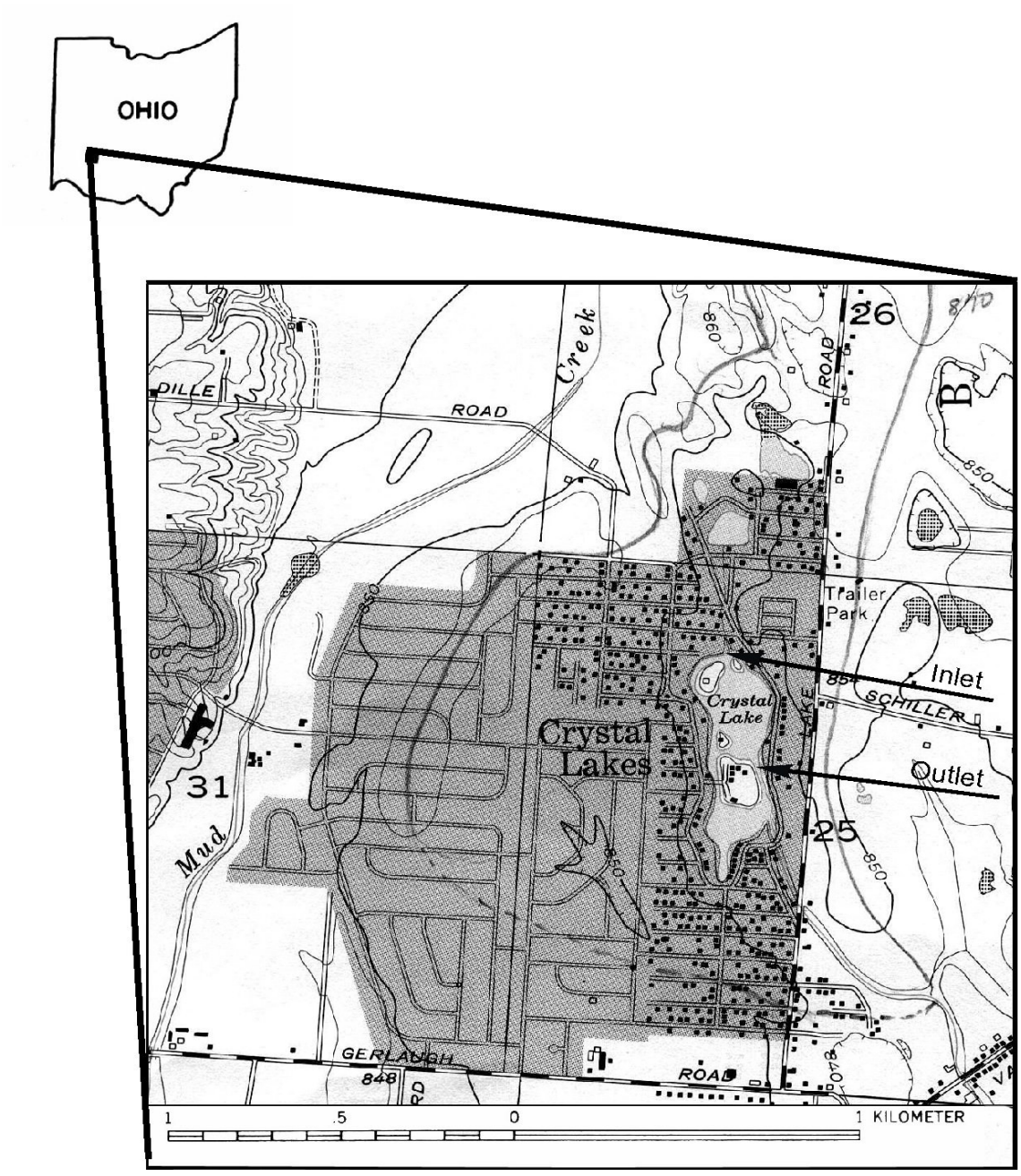

Figure 1. Location of Crystal Lake. The study site is the portion of the lake labeled as "Crystal Lake" between the inlet and the outlet.

According to an Ohio EPA study (Talsna, 1975), Crystal Lake (Fig. 2) is stream fed, which has a large affect on its physical, chemical, and biological activity. The outlet of Crystal Lake flows through a swampy area to the Mad River two kilometers away. The

drainage basin of the lake is about 5 km^2, with a majority of the basin being tilled farmland (Talsna, 1975). Clark County gets an average of 38 inches of rain annually (Norris et al., 1952).

Crystal Lake is surrounded by residential and agricultural areas and is used for recreational purposes. A portion of the lake was once a bass/bluegill fishery (Talsna, 1975). The lake is eutrophic, meaning that the nutrients are high, photosynthesis is high, and the hypolimnion is anaerobic. However, Secchi depth indicated that Crystal Lake is less eutrophic than near-by Kiser and Acton Lakes (Talsna & Lazorchak, 1975). All homes surrounding the lake are connected to a public sewer system (Collins, 1999).

Figure 2. View of Crystal Lake from fishery. Public beach and clubhouse can be seen.

2.1.2 Formation of Crystal Lake

Crystal Lake was formed by the retreat of Wisconsian glaciers between 15,000-12,000 years ago (Woodruff, 1999). During this time, the western half of Clark County was covered by ground moraine deposited by the Miami lobe of a retreating glacier during the Wisconsian stage of glaciation (Winter, 1997). The Teays drainage system in the Late Tertiary formed the buried valley and outwash plain that Crystal Lake lies in (Goldthwait, 1952). A study of the ^{14}C of a peat layer in a nearby marl deposit also indicate that the soil is of glacial origin (Clemens, 2001).

There are two theories as to which glacial process formed Crystal Lakes. One theory is that Crystal Lake is a kettle lake. Kettle lakes form when blocks of ice break off during glacial retreat; these blocks melt over hundreds of years and form depressions that fill with water. Because of irregularities in the ice blocks that form them, kettle lakes have irregular shapes, slopes, and depressions (Wetzel, 2001). The shape of Crystal Lake indicates that it is a kettle lake.

Another more recent theory is that Crystal Lake is a moulin-induced scarp. A moulin is a hollow crevasse that allows surface water to flow vertically through a glacier. This flowing water can displace soil beneath glaciers and form a series of lakes, which line up in a row (Cheng, personal communication). Crystal Lake lines up with nearby small lakes, indicating that it is moulin-induced.

2.1.3 Previous studies

A study by Collins (1999) on Crystal Lake has indicated that the lake is thermally stratified between the spring and fall, and overturns twice a year: once in the early spring, and once in the late fall/early winter. There is also little interaction between the lake water and groundwater in the area. Through carbon-isotope analysis, Woodruff (1999) found that Crystal Lake is affected slightly by calcite precipitation and dissolution,

but much more by photosynthesis and decomposition. It was also discovered that in July of 1998, photosynthesis was occurring between 2.5-5 m. Clemens (2001) studied the formation and sediments of Crystal Lake. He verified through ^{14}C analysis of a peat layer that Crystal Lake was not man-made; he also found that most of the lake bed is calcareous mud, and that low pH at depth could prevent lithification of sediment.

2.2 Limnology

In many lakes, there is a notable temperature difference between the surface and bottom in warmer seasons. The upper layer, called the epilimnion, is mixed by surface winds, and it is typically warmer than other layers within the lake. The hypolimnion is the lowest thermal layer, and is often colder than the epilimnion. Between the epilimnion and hypolimnion is the metalimnion; this layer is not uniform in temperature. Rather, it is the thermal gradient between the other layers. The thermocline, located within the metalimnion, is the plane with the maximum rate of temperature change. When the above described layers are well defined, the lake is said to be stratified. Typically, there are two periods a year that a temperate lake is stratified, punctuated by two periods of mixing (Wetzel, 2001). Mixing, or overturn, occurs when the temperature of the epilimnion becomes close to the temperature of the hypolimnion (Drever, 1997).

In the spring, surface water heats faster than the water can be mixed by wind, causing stratification. The uppermost portion of the lake, being warmer and therefore less dense, remains on the surface as a separate layer while the cooler, denser water remains near the bottom. In the later summer or early fall, the surface water begins to cool, becoming more dense. This causes the water to circulate deeper, and results in mixing of the entire water column, or the fall turnover. During winter stratification, the surface temperature becomes colder than the layers below. However, ice cover often prevents mixing, resulting in an inverse stratification. During the early spring, when the

ice cover melts, the water column mixes again. Since the temperatures in the epilimnion and hypolimnion are very similar, only a small amount of wind is required to cause the spring turnover. Lakes that have a small surface area, such as Crystal Lake, tend to have short periods of overturn (Wetzel, 2001).

The photic zone is the depth of water in a lake that light is able to penetrate. The intensity of light diminishes with depth, depending on the amounts of suspended solids, such as clays and microorganisms (Scheffer, 1998). The photic zone is defined as twice the Secchi depth (Winter, 1997). Secchi depth is an indication of turbidity, but different sources of turbidity cause differences in light attenuation. For example, if turbidity is due to suspended clay, light attenuation would be less than if turbidity was caused by phytoplankton (Scheffer, 1998). Secchi depth is measured with a Secchi disk: a round disk divided into two black and two white triangles. The disk is lowered into the water until the separate colors can no longer be distinguished.

The oxidation-reduction potential, or ORP, is a measure of the potential difference in a solution between an inert indicator electrode and a standard hydrogen electrode (Eaton et al., 1995). In other words, it is a measure of the electron activity of a solution. If the ORP is positive, a solution is oxidizing; if it is negative, the solution is reducing. Predominant redox reactants are carbon, oxygen, nitrogen, sulfur, iron, and manganese. As the amount of oxygen decreases, electron activity decreases, and the ORP drops (Wetzel, 2001). Redox conditions are largely controlled by the processes of photosynthesis and bacterial decomposition of organic matter (Drever, 1997).

2.3 Geochemistry

Typical major ions in natural water include Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, HCO_3^{-}, SO_4^{2-}, and Cl^{-}. Since Crystal Lake is located within a carbonate terrain, the dominant ions are Ca^{2+}, Mg^{2+}, and HCO_3^{-}. In aquatic biological studies, nitrogen, silica, and phosphorus are also important nutrients to consider.

Sources of sulfur include rocks, fertilizers, and atmospheric precipitation. The predominant form of sulfur in lake water is sulfate (SO_4^{2-}). During decomposition, sulfate is reduced to hydrogen sulfide by sulfur-reducing bacteria (Wetzel, 2001). This reaction is shown in below in Equation 1 (Drever, 1997).

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^{-} \quad (1)$$

Sulfur-reducing bacteria are anaerobic, and, as seen from the above equation, they use sulfur as an electron acceptor during metabolism. The primary sulfur-reducing bacteria in a eutrophic lake include *Pseudomonas liquefaciens* and *Bacterium delicatum* (Wetzel, 2001). However, these bacteria in Crystal Lake have not yet been identified. In aerobic areas, any hydrogen sulfide that may be present is rapidly oxidized, and therefore is not often detected (Wetzel, 2001). However, even small amounts of dissolved H_2S can be toxic to fish (Eaton et al., 1995).

The two most common forms of nitrogen found in eutrophic lakes are nitrate (NO_3^{-}) and ammonium (NH_4^{+}). Nitrate is often found in surface layers where aerobic conditions exist, and is used by algae as a nutrient. Under anaerobic conditions, however, nitrate reduction can occur. During this process, certain bacteria use nitrate as an electron acceptor to oxidize carbon to CO_2, creating ammonium (Drever, 1997).

Silica (SiO_2) is important when studying algae because it is used by a type of algae, called diatoms, as part of their cell walls. The availability and distribution of silica can have a strong influence on the overall pattern of algal succession and productivity of lakes. In areas where diatoms are present, the amount of silica remaining in the water

column is less. As these diatoms settle to the lake sediments, the silica of their cell walls will start to dissolve with the decreasing pH (Wetzel, 2001). This often results in an increase in silica concentrations with depth.

The concentration of phosphorus in water is very important when conducting a biological assessment. It is often the limiting nutrient for organisms because phosphorus is essential for growth (Eaton, et al, 1995). The phosphorus level can influence phytoplankton biomass and chlorophyll content (Koreva & Mineeva, 1996). In natural waters, phosphorus is most often in the form of phosphates (PO_4^{3-}) (Eaton, et al, 1995). These phosphates can either occur naturally or enter waters from fertilizers (Scheffer, 1998).

The concentration and distribution of the above ions and nutrients can have significant effects on the microorganisms, and vice versa. For example, concentrations of calcium over 30 mg/L and magnesium over 10 mg/L can suppress photosynthesis (Wetzel, 2001). On the other hand, algal uptake of nutrients will decrease the concentrations within the water column. Algae use nitrogen for amino acids and proteins, phosphorus for nucleotides, silica for the walls of diatoms, sulfur for amino acids, calcium for cell walls, and chloride, potassium, sodium, and magnesium for intracellular ion balance regulation. Algae that are not ingested slowly sink to the bottom and are degraded. This releases nutrients back into the hypolimnion (Sigee, 2005). There is also a continuous loss of nutrients from the epilimnion to the hypolimnion in the summer (Scheffer, 1998).

Dissolved oxygen is a measure of the amount of free oxygen in the water. This oxygen can come from photosynthesis, or from atmospheric dissolution (Drever, 1997). Dissolved oxygen levels depend on physical, chemical, and biochemical activities. Dissolved oxygen is measured by using a membrane electrode potential to detect the rate of diffusion of molecular oxygen across the membrane (Eaton et al., 1995). If there

is dissolved oxygen present, the area is termed oxic, or aerobic. If no or very small amounts of dissolved oxygen is present, the area is anoxic, or anaerobic. Photosynthesis increases dissolved oxygen (Equation 2), while decomposition and respiration decrease dissolved oxygen (Equation 3) (after Drever, 1997).

$$106\ CO_2(aq) + 16\ NO_3 + HPO_4^{2-} + 122\ H_2O(aq) + (\text{trace elements, energy}) =$$

$$C_{106}H_{263}O_{110}N_{16}P + \mathbf{138\ O_2} \qquad (2)$$

$$CH_2O + \mathbf{O_2(aq)} \rightarrow CO_2(aq) + H_2O \qquad (3)$$

One of the most common measurements taken in natural waters is pH, which is a measure of proton [H^+] activity. Sources of acidity include uncombined carbon dioxide, organic acids, mineral acids, and salts of strong acids and weak bases (Wetzel, 2001). Changes in carbon dioxide seem to have the most drastic affect on pH.

Photosynthesis and respiration are major factors that affect the concentration of carbon dioxide in water (Wetzel, 2001). During photosynthesis, carbon dioxide is consumed, once again illustrated in Equation 2.

$$\mathbf{106\ CO_2(aq)} + 16\ NO_3 + HPO_4^{2-} + 122\ H_2O(aq) + (\text{trace elements, energy}) =$$

$$C_{106}H_{263}O_{110}N_{16}P + 138\ O_2 \qquad (2)$$

This decrease in carbon dioxide will increase pH.

Carbon dioxide produced from decomposition can accumulate in the hypolimnion (Wetzel, 2001), which is partially responsible for the decrease in pH with depth that is commonly seen. Other sources of this pH decrease with depth include oxygen, sulfate, and nitrate.

Another source of carbon dioxide in natural waters is from the atmosphere. In 1991, carbon dioxide in the atmosphere was about 0.0355%, and is increasing (by volume) by ~0.2% per year. Most lakes are super-saturated with carbon dioxide, meaning that there is more carbon dioxide dissolved in lakes than exists in the atmosphere. Other factors can affect the amount of carbon dioxide in lakes, such as

temperature and alkalinity. The solubility of carbon dioxide decreases as the temperature increases, while the solubility of carbon dioxide increases in alkaline water (Wetzel, 2001).

2.4 Carbon Isotope Fractionation

The isotopes of interest in this study are the two stable carbon isotopes: ^{12}C and ^{13}C. ^{12}C comprises nearly 98.9% of all carbon species, and ^{13}C comprises about 1.1% of carbon (Hoefs, 1997). The carbon isotope composition is reported as part per thousand (‰) of the difference in ratios of two stable isotopes normalized to a standard; for carbon:

$$\delta^{13}C\ (‰) = \{[(^{13}C/^{12}C)_{sample}-(^{13}C/^{12}C)_{V\text{-}PDB}]/(^{13}C/^{12}C)_{V\text{-}PDB}\}^* 1000 \qquad (8)$$

The standard originally used for carbon isotopes was taken from the internal calcite structure of the fossil *Belemnitella americana* from the Cretaceous-aged PeeDee Formation in South Carolina; this standard is referred to as PDB. Over the years, this reference has been exhausted, and a new international standard was redefined in Vienna, Austria, which is referred to as V-PDB (Hoefs, 1997). The more positive the $\delta^{13}C$ value, the more enriched it is in ^{13}C (Clark & Frtiz, 1997). There are many processes which affect the fractionation of carbon in aqueous systems, such as photosynthesis, dissolution and precipitation of calcite, and the decay of organic matter (Woodruff, 1999). Typical carbon isotope compositions are listed in Table 1.

Type of Carbon	Measured Isotope Composition
Marine Carbonate	~ 0‰
Marine Calcite/Aragonite	0.9-2.7 ‰
Organic Matter	~25 ‰
Plants	-8.5 to -30 ‰
Amospheric CO_2	-5.5 to -8.5 ‰
Groundwater DIC	0 to -21 ‰
Freshwater carbonate	-17 to +5 ‰
Biogenic CH_4	-41 to -80 ‰

Table 1- List of Fractionation Values of Various Carbon Sources, taken from Hoeffs, 1997

One of the major processes of carbon isotope fractionation is photosynthesis, where algae in the water column take in aqueous CO_2 to form biomass (Bade, et al, 2006), as shown in the equation below:

$$106\ CO_2(aq) + 16\ NO_3 + HPO_4^{2-} + 122\ H_2O(aq) + (\text{trace elements, energy}) =$$

$$C_{106}H_{263}O_{110}N_{16}P + 138\ O_2 \qquad (2)$$

(Drever, 1997). During this process, algae preferentially use the lighter carbon isotope, ^{12}C. This results in the residual water column becoming enriched in ^{13}C, increasing the $\delta^{13}C$ value. The average fractionation during photosynthesis is about 13 ‰ V-PDB (Bade et al., 2006).

The magnitude of carbon fractionation by photosynthesis depends greatly on the type of algae. Within a carbonate setting, some algae may also use carbon in the form of $HCO_3^-(aq)$, which is about 8‰ enriched in ^{13}C as opposed to $CO_2(aq)$. Differences can also result from differences in lipid, polysaccharides and proteins in different species (Bade et al., 2006). Carbon fractionation during photosynthesis also depends on

temperature, nutrient availability, and volume-to-surface ratio of organisms (Global, 2003).

Other factors that affect carbon fractionation are carbonate dissolution, carbonate precipitation, decomposition, and methanogenesis. The dissolution of carbonate species introduces heavy carbon into the aqueous system. Precipitation of carbonate will decrease the amount of heavy carbon in water. During the decomposition of isotopically-light organic matter, light carbon is reintroduced into the system. The process of methanogenesis uses light carbon, resulting in the enrichment of heavy carbon in the water column, while the oxidation of the light methane will reintroduce light carbon back into the water column (Drever, 1997).

2.5 Lake microbiota

2.5.1 Algae Overview

Planktonic algae, also called phytoplankton, are eukaryotic, photosynthetic aquatic organisms. They exist in all environments; phytoplankton productivity makes up 40-50% of the total global primary productivity (Young & Beardall, 2005). Different types and amounts of algae can influence water quality, such as color, pH and odor (Eaton et al., 1995). Since all algae photosynthesize, they require light, and can only live in the photic zone of lakes. The intensity of light required for algal photosynthesis increases as temperature increases (Wetzel, 2001). All types of algae photosynthesize using water as their electron donor; however, some can also utilize H_2 as an electron donor (Madigan et al., 2003). Several factors that affect growth and succession of phytoplankton include light, temperature, buoyancy regulation, inorganic nutrient availability, organic micronutrient availability, and competition (Wetzel, 2001). In this study, the term ‘algae’ is used to refer to both phytoplankton and blue-green algae.

One factor that has helped algae become so successful is the fact that most types of algae can migrate through the water column, horizontally or vertically, in response to light and nutrient availability, temperature, and pH. Some species shift their position every day, called diel vertical migration (Bernot et al., 2004). Algae have to respond quickly to environmental changes because of their short life cycles (Eaton et al., 1995).

2.5.2 Types of Algae

There are several main types of algae of interest to this study. Cyanobacteria, commonly known as blue-green algae, are not truly algae. They are prokaryotes, and have no nuclei, chloroplasts, or organelles (Scheffer, 1998). However, cyanobacteria are often called algae because they photosynthesize. Cyanobacteria and algae have evolved very differently. Cyanobacteria do not need vitamins; they use either nitrate or ammonium for their nitrogen source. Being photosynthetic, most species are obligate phototrophs, meaning that they require sunlight (Madigan et al., 2003). The amount of cyanobacteria is very important in characterizing phytoplankton communities because they affect the amounts of sunlight and vital nutrients available for other phytoplankton (Scheffer, 1998).

Another very common type of algae is diatoms. Diatoms first appeared ~190 million years ago (Rothplez, 1896). Their cell walls are composed of silica. These external walls are called frustules, which restrict decay and increase preservation potential (Madigan et al., 2003). Of the roughly 600 living and fossil diatom genera, about 17% are from freshwater environments (Prothers, 2004).

In a eutrophic lake, diatoms are most common, especially *Asterionella sp., Fragilaria crotonensis, Melosira granulatea,* and species of *Synedra* and *Stephanodiscus* (Wetzel, 2001). The phytoplankton community of lower zones of a lake is typically

comprised of diatoms (Sarvala et al., 2003), and they generally make up the base of the freshwater food pyramid. Diatoms are important because they are sensitive to their environment; therefore they are good indicators of paleoclimate, paleoceanography, pH changes, and show sufficient paleo-concentrations of silica, nitrate, and phosphate (Prothers, 2004). Another reason that diatoms are useful is because of their abundance, ease of preservation, and ease of identification through frustules (Wetzel, 2001).

Another common form of algae is the green algae. Green algae often comprise a significant portion of phytoplankton communities. Green algae, along with cyanobacteria, are common during warm periods (Wetzel, 2001). Several types of green algae can also incorporate carbonate into their cell walls. A type of calcareous green algae, the Charophytes, has been found in cores of Crystal Lake sediments (Clemens, 2001).

2.5.3 Photosynthesis

The process of photosynthesis uses carbon dioxide or bicarbonate as a carbon source for biosynthesis, as shown in Equation 2 (Drever, 1997).

$$106\ CO_2\ (aq) + 16\ NO_3 + HPO_4^{2-} + 122\ H_2O\ (aq) + (\text{trace elements, energy}) = C_{106}H_{263}O_{110}N_{16}P + 138\ O_2 \quad (2)$$

Since photosynthesis consumes carbon dioxide, the pH increases, which may lead to the precipitation of carbonate mud (Wetzel, 2001). Photosynthesis can sometimes be facilitated by the uptake of dissolved inorganic carbon (DIC), which increases the amount of carbon dioxide within cells. The creation of this concentration gradient improves the efficiency of carbon fixation (Young & Beardall, 2005).

2.5.4 Chlorophyll

Photosynthesis occurs in molecules called chlorophyll. In plants, chlorophyll is held within organelles called chloroplasts. There are three main types of chlorophyll pigments: chlorophyll a (C_a), chlorophyll b (C_b), and chlorophyll c (C_c). Of these, chlorophyll a and chlorophyll b are the most common (Madigan et al., 2003). Chlorophyll a is only type of chlorophyll that is directly involved in the light reactions of photosynthesis. When light is absorbed by other types of chlorophyll, the energy is then transferred to chlorophyll a pigments (Campbell & Reece, 2002). There are also a variety of accessory pigments of chlorophyll (Bianchi, 2002). Photosynthetic organisms have been classified by the types of these pigments (Table 2) (Faust & Norris, 1982).

Type of Organism	Common Name	Type of Chlorophyll	Accessory Pigments
Cyanobacteria	Blue-green algae	a	zeaxanthin, echinenone
Chlorophyta	Green algae	a, b	lutein
Chrysophyta	Diatoms	a, c	fucoxanthin
Phaeophyta	Brown algae	a, c	

Table 2- Classification of algal groups by chlorophyll pigments (Madigan et al., 2003)

All green plants have chlorophyll a, which makes up 1-2 % of dry weight of algae (Eaton et al., 1995). Because of this, chlorophyll a is often used to estimate algal biomass (Méléder et al., 2003).

3.0 Methodology

3.1 Field work

Water samples were collected from different depths and analyzed for their nutrient and chlorophyll content, as well as carbon isotopes. These analyses were conducted using several methods, including mass spectrometry, spectrophotometry, and ion chromatography. All measurements *in situ* were taken at a single location at 1.5 meter intervals, and water samples were collected from each interval for laboratory analysis. Samples were taken once a month in May 2007, June 2007, July 2007, twice in August 2007, and three times in October 2007.

Measurements taken *in situ* for this study were done using a YSI 6600 multi-probe sonde, which measures specific conductance, pH, temperature, dissolved oxygen, and redox potential. Turbidity measurements were taken at several sample times using a Secchi disk.

Water samples were collected from depth using a submersible pump connected to plastic tubing. At each sample interval, 120 mL of water was collected for chlorophyll analysis. Sample bottles were immediately wrapped in aluminum foil to prevent exposure to sunlight, and filtered once taken to the laboratory. For carbon isotope analysis, between 30-60 mL of sample was collected. An additional 120 mL were collected from each sample interval for ion analysis and filtered *in situ*.

3.2 Lab Work

Samples at deeper locations were tested for sulfide using a Hach sulfide kit. Samples were selected for sulfur analysis based on odor. Sulfide has a very distinct odor, similar to that of rotten eggs. A sulfide concentration of as low as 0.025-0.25 µg/L

results in a detectable odor (Eaton et al., 1995). Analysis was done immediately after returning to laboratory since sulfide is rapidly oxidized.

Samples for carbon isotope analysis were precipitated as strontium chloride and analyzed at the Environmental Isotope Laboratory, University of Arizona. Glass bottles were filled with roughly 100mg of strontium chloride ($SrCl_2$) and 0.5 mL of carbonate-free 10N sodium hydroxide (NaOH) and placed in a desiccator connected to a vacuum. The evacuated bottles were capped with butyl rubber to preserve vacuum and for later sample injection. Water samples were filtered and injected into the evacuated bottles using a syringe when collected (Fig. 3).

Figure 3- Carbon sample collection. Photo by William Jones.

The high pH caused by the added NaOH will force all dissolved inorganic carbon (DIC) to be in the form of carbonate; all $carbonate_{(aq)}$ will react with $SrCl_2$ to form solid strontium carbonate ($SrCO_3$), which will precipitate from the solution. These reactions are shown below (Hoefs, 1997).

$$HCO_3^- + NaOH \rightarrow CO_3^{2-} + Na^+ + H_2O \quad (9)$$

$$CO_3^{2-} + SrCl_2 \rightarrow SrCO_3 + 2Cl^- \quad (10)$$

Once the samples were collected and transported to the laboratory, the tubes were centrifuged and decanted, and the $SrCO_3$ dried in a dessicator connected to a vacuum. Barium chloride has been used for the precipitant in previous studies. However, strontium chloride is less hazardous. The dried $SrCO_3$ was sent to the University of Arizona for carbon isotope analysis using a mass spectrometer.

Alkalinity titrations were performed and analyzed using Gran's plotting techniques, as described in Drever (1997). This is often considered the most accurate measure of alkalinity. A Gran plot identifies the point at which all of the alkalinity has been titrated and a build-up of hydrogen ions begins. Once the end points were determined, alkalinity was calculated using the below equation (Drever, 1997).

$$\text{Alkalinity in mN } HCO_3^- = (N*Vs)/A \quad (11)$$

$$\text{Alkalinity in mg/L } HCO_3^- = \text{mN } CO_3^{-}*61 \quad (12)$$

where A = mL of acid used and N = normality of acid (Cheng, personal communication).

The Gran plots created during alkalinity titrations are located in the appendices. Before analysis, the water samples were filtered using a 47-mm GF/F glass fiber filter with a 0.22-µm pore size.

Water samples taken back to the laboratory were analyzed for nitrate, silica, and chlorophyll using a spectrophotometer, which directs beams of light of different wavelengths through a solution of pigments and measures the fraction of light transmitted at each wavelength (Eaton et al., 1995). Before analysis, the samples were filtered using a GF/F glass fiber filter with a .22 µm pore size. This pore size is preferred for separating suspended solids. Glass filters were used because they are preferred for chlorophyll analysis, to be discussed later. However, since a glass fiber filter was used, traces of silica from the glass were added to the filtered samples. To correct for this, 120 mL of distilled water was filtered, which is equivalent to the amount of sample filtered.

The silica content of the distilled water was then measured. This process was repeated three times, yielding an average amount of 0.8 mg/L. This value was subtracted from the measured values of silica.

Ion analysis was conducted using an ion chromatograph, or an IC. A Dionex ICS 2000 ion chromatograph was used to measure the amounts of typical anions and cations in the water. IC analysis provides a single technique for rapid, accurate measurement of ion concentrations. Samples used for IC analysis must be filtered to remove all particles greater than 0.2 µm. The samples for this research were filtered *in situ* through a 0.22 µm filter. Samples collected for cation analysis were also acidified to prevent adsorption to the container wall or precipitation.

3.3 Algae identification

Algae identification and algal counts were attempted in this study. However, this was not possible because the cells were fragmented and crumpled by the motorized submersible pump during collection. In spite of this, samples were collected with the hope of carbon isotope analysis on the algal biomass. Unfortunately, insufficient sample volume was collected for a proper amount of dry biomass to be sent out for carbon isotope analysis.

3.4 Chlorophyll analysis

For chlorophyll analysis, water samples were passed through a glass filter, which was then soaked in a saturated magnesium carbonate/acetone solution to remove the pigments. The effluent was analyzed with a spectrophotometer to determine the amounts present. This information was used to aid in algae identification.

Chlorophyll molecules could be rapidly degraded by sunlight (Eaton et al., 1995). To avoid degradation, sample bottles were wrapped in aluminum foil as soon as they were collected in the field. Once back in the laboratory, the samples for chlorophyll analysis were passed through a GF/F glass filter with a 0.22 µm pore size under little light. Glass fiber filters are preferred for chlorophyll analysis because the fibers help break algal cells during maceration (Eaton et al., 1995), which allows for more accurate results. The filters were then covered with aluminum foil, labeled, and frozen until analysis. Research has shown that filters can be stored frozen for at least three months without affecting the results of chlorophyll analysis (Méléder et al., 2003).

Chlorophyll analysis was conducted based on the Standard Methods (Eaton et al., 1995). After filtration, a solution of saturated magnesium carbonate was prepared by mixing 1 g $MgCO_3$ with 100 mL of DI water. Then, a 90% aqueous acetone solution was prepared by mixing 90 parts acetone with 10 parts of the saturated magnesium carbonate solution. The filters were then placed in a mortar and covered with 2-3 mL of 90% aqueous acetone solution, then macerated using a mortar and pestle. The filter slurry from the mortar was transferred to centrifuge tubes; the mortar and pestle were then rinsed with the acetone solution and added to sample slurry. This ensured that the maximum amount of chlorophyll was collected from each filter. The centrifuge tubes were then centrifuged for ~5 minutes and decanted for analysis using a spectrophotometer.

In order to calculate the concentrations of each chlorophyll pigment- C_a, C_b, and C_c - the maximum absorbance spectra of each pigment were used (Faust & Norris, 1982). The optical densities were measured at wavelengths of 750 (turbidity), 664 (C_a), 647 (C_b), and 630 (C_c) nm. The measured result from 750 was subtracted from each reading before any calculations were performed. Based on the optical densities,

calculations where then performed for each sample. The calculations used are shown below (Eaton et al., 1995).

C_a mg/L = 11.85(OD 664) - 1.54(OD 647) - .08(OD 630) (13)

C_b mg/L = 21.03(OD 647) - 5.43(OD 664) - 2.66(OD 630) (14)

C_c mg/L = 24.52(OD 630) - 7.6(OD 647) - 1.67(OD 664) (15)

Chl x mg/m^3 = (C_x * extract volume (L)) / Volume of sample (m^3) (16)

Biomass (mg/m^3) = C_a * 67 (17)

Results from these calculations are listed in the Appendices.

The above calculations may under- or over- estimate chlorophyll a. This is due to the overlap of the absorption bands of the chlorophyll accessory pigments, which may affect the spectrophotometric readings of chlorophyll a (Eaton et al., 1995).

4.0 Results and Discussion

4.1 Limnology

As previous studies have illustrated, Crystal Lake is almost a 'textbook' thermally stratified, eutrophic lake. There is a sharp temperature contrast between the epilimnion and the hypolimnion for all sample dates (Fig. 4). The temperature of all layers increase between May and July; the temperature of the epilimnion decreases between July and October. The depths of the epilimnion are similar between May and July, illustrating the mature development of stratification. However, in October, the depth of the epilimnion is greater, and the temperature gradient is decreasing. The temperature of the metalimnion and hypolimnion are also greatest in October. The temperature of the hypolimnion progressively increased from May to July to October. The source of heat could be either heat flux from underlying sediments or influx of groundwater. Further study is needed to verify the heat source. Stable isotope composition of water near the sediment-water interface could reveal whether the is a groundwater influx.

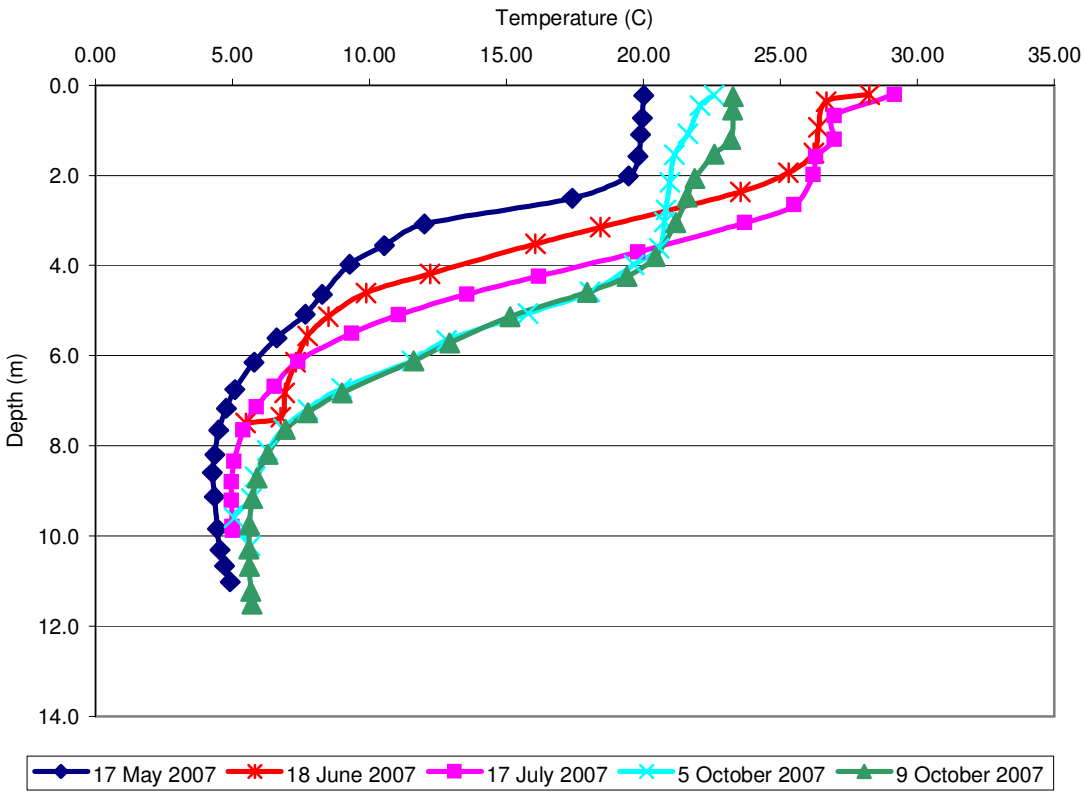

Figure 4- Temperature variations with depth over time

There is an overall decrease in specific conductance over time (Fig. 5), which is partially from the intake of ions by algae. The increase in pH caused by photosynthesis also causes calcium carbonate to precipitate, and lower the specific conductance in the epilimnion and metalimnion. In the hypolimnion, decay of organic matter generates CO_2 and lowers the pH. Consequently, the lower-pH water in the hypolimnion causes the re-dissolution of carbonate that was precipitated from either the epilimnion or metalimnion. There is also a constant loss of nutrients from the epilimnion to the hypolimnion due to the decay of organic matter in the hypolimnion that releases nutrients.

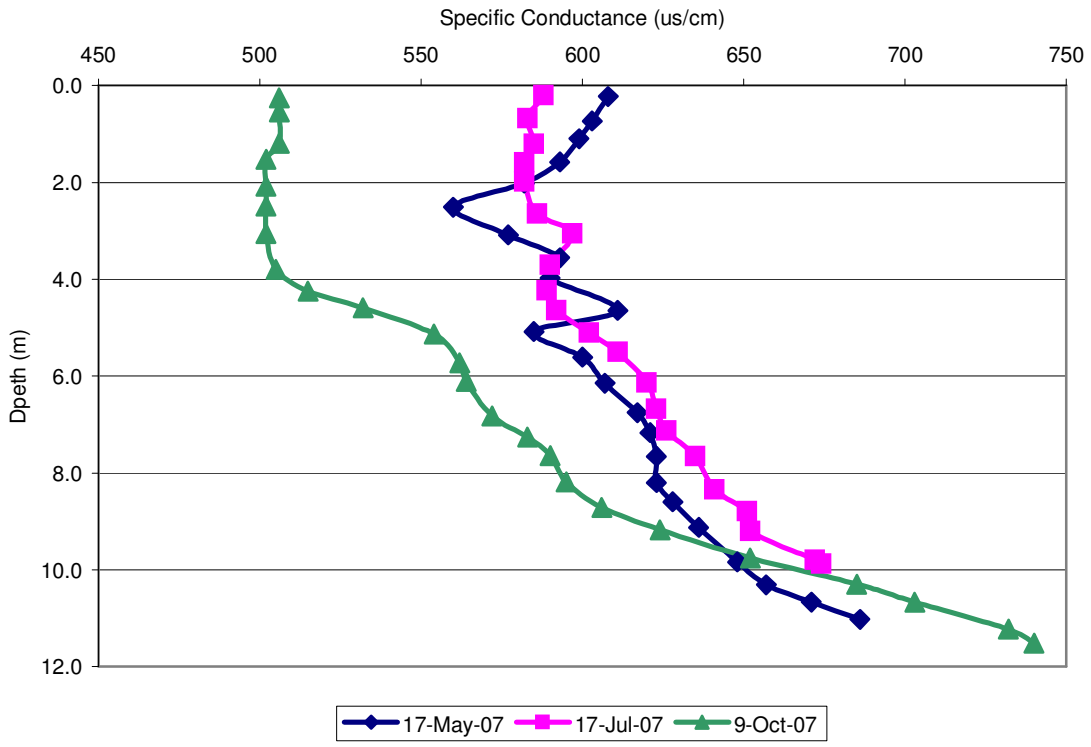

Figure 5- Specific conductance with depth over time

Dissolved oxygen is highly stratified in Crystal Lake (Fig. 6). The concentration of dissolved oxygen is similar in the epilimnion, with a slightly lower surface value in July when the temperature is warmest. The solubility of oxygen decreases with increasing temperatures, so this was expected. The concentrations in the epilimnion are from either the photosynthetic production of oxygen and equilibration with the atmosphere, or only from equilibration with the atmosphere.

There is a great increase in dissolved oxygen concentrations in the metalimnion. This is from the production of oxygen during photosynthesis. The amount of dissolved oxygen decreases between May and July and increases in October, indicating that the rate of photosynthesis is higher in May and October. This is confirmed by chlorophyll analysis, discussed in Section 4.3. Dissolved oxygen values decrease very rapidly in the hypolimnion, due to the respiration of bacteria.

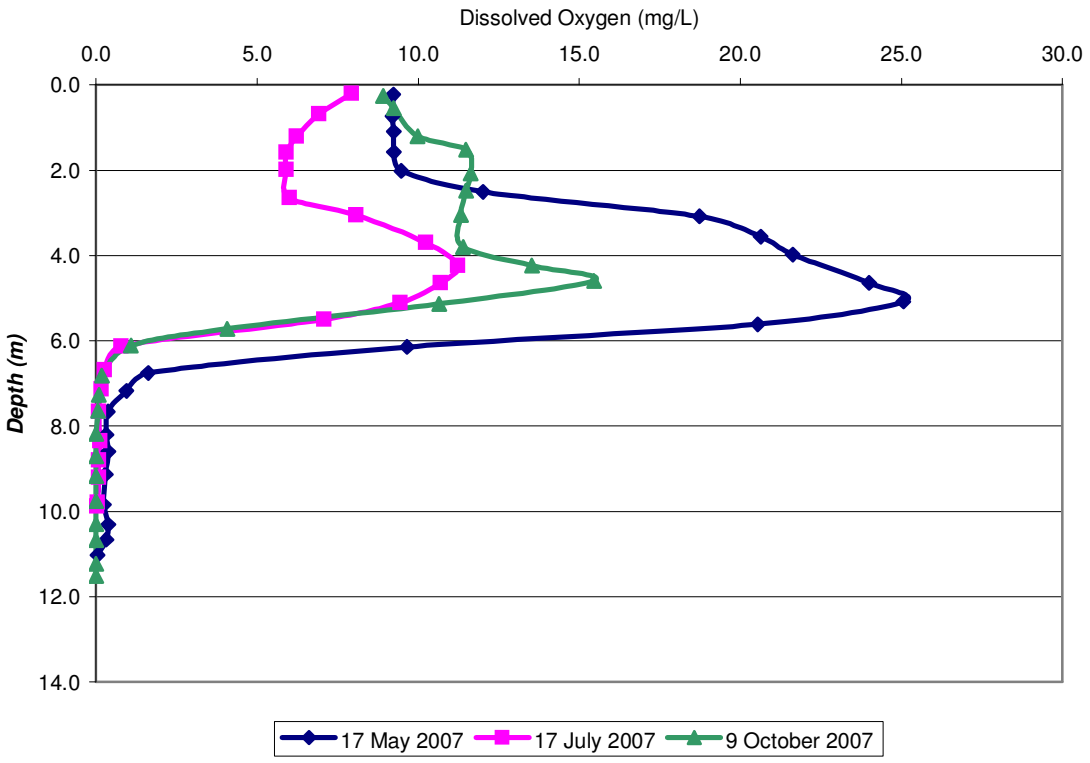

Figure 6- Dissolved oxygen with depth over time

In Crystal Lake, pH is stratified (Fig. 7). The pH in the epilimnion is consistently high, while in the hypolimnion, the pH is low. In May, there is a marked increase in pH in the metalimnion; this is a result of photosynthesis in this layer. A similar pattern is seen in October, but is not as defined. In July, the pH in the epilimnion is the highest. The effect of photosynthesis in the metalimnion (a sharp increase in pH) is also not visible in July. This is because the epilimnion is significantly warmer in July than at any other time. Carbon dioxide is less soluble at warmer temperatures; this decrease in aqueous carbon dioxide caused the high pH in July.

In the hypolimnion, the pH decreases significantly, mainly from the decomposition of biomass and the production of carbon dioxide during respiration. However, in July, there is an increase in pH at depth. This may be from the presence of

carbonate. The high pH in the epilimnion at this time could be a result of carbonate dissolution, which consumes H^+. However, this hypothesis is consistent with what is observed for the months of May and October; both months have high specific conductance from carbonate dissolution, but remain at a lower pH value. Field instrument malfunction is a possibility for the pH trend in July.

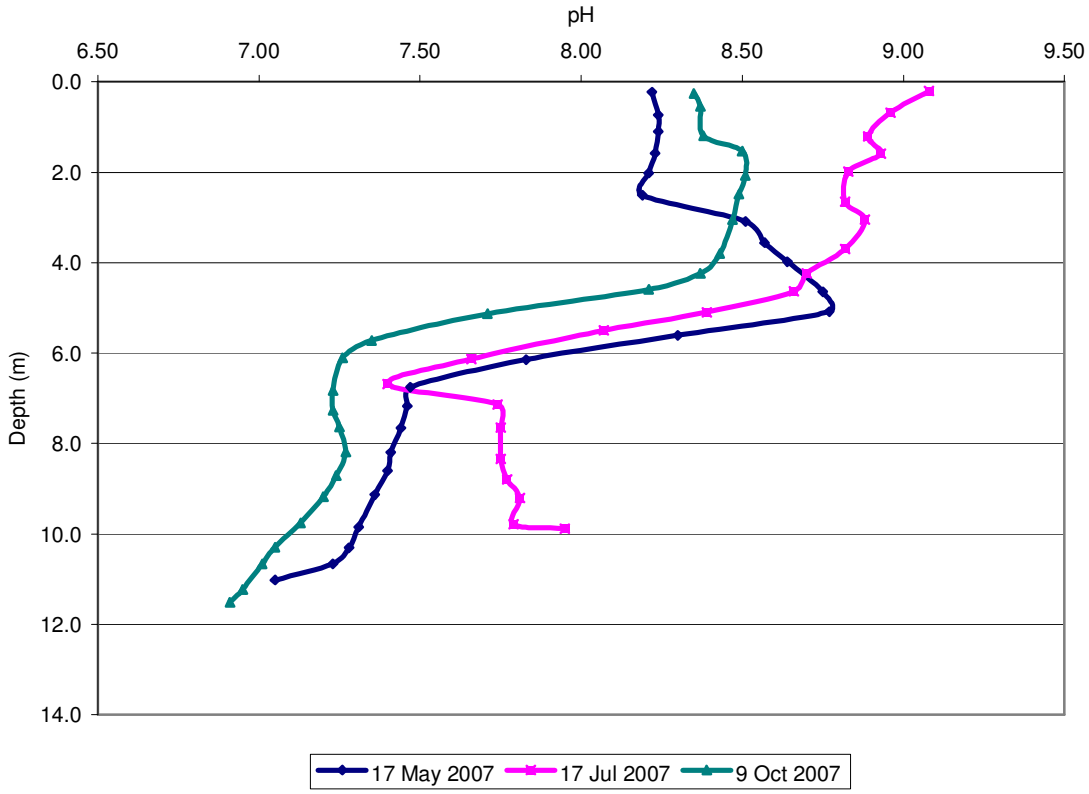

Figure 7- pH with depth over time

It was expected that alkalinity values would increase with depth, and show a similar trend to those observed with specific conductance. However, the alkalinity data is not consistent with other data (Fig. 8). This may be a result of human error during analysis; several groups were involved in conducting alkalinity titrations, and differences in their techniques and precision may have caused erroneous values of alkalinity in Crystal Lake.

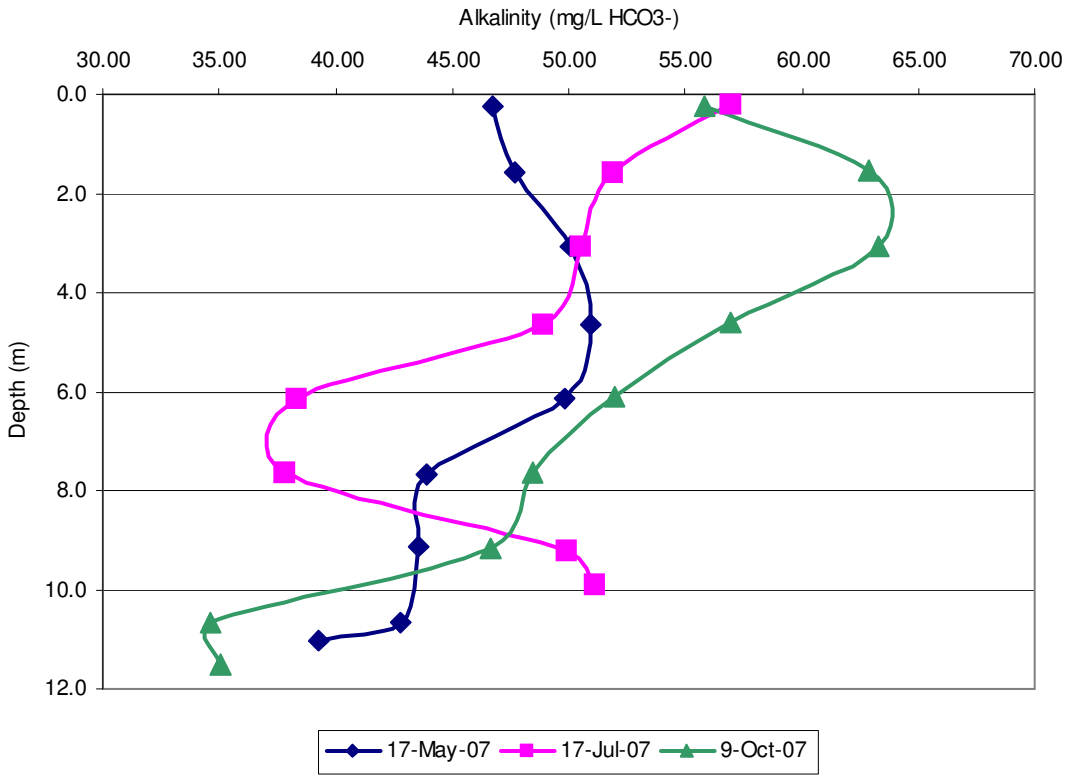

Figure 8- Alkalinity with depth over time

4.2 Ion analysis

In Crystal Lake, sulfide levels increased with depth and over time. Since sulfide is related to the decomposition of biomass, one would expect a correlation between these two variables. The highest amounts of biomass were recorded in May (discussed in more detail in Section 4.3), while the highest recorded values of sulfide occurred in October (Fig. 9). It takes time for the biomass to settle to the depths of the lake where decomposition can occur, so a lag between the peak biomass and peak sulfide was anticipated; the increase in decomposition of biomass over time caused the increase in sulfide over time.

A sulfide odor was detected from the bank of the lake all three sampling days in October. However, surface samples did not indicate any sulfide present. The odor may

have been from decomposition occurring in layers of mucky, peat-like soils in the shallowest sections of the lake; these areas are likely anaerobic just below surface. This apparent increase in decomposition near the shore could indicate biogeochemical changes within the shallow sediments, which may also be an indication of a pending turnover of the lake.

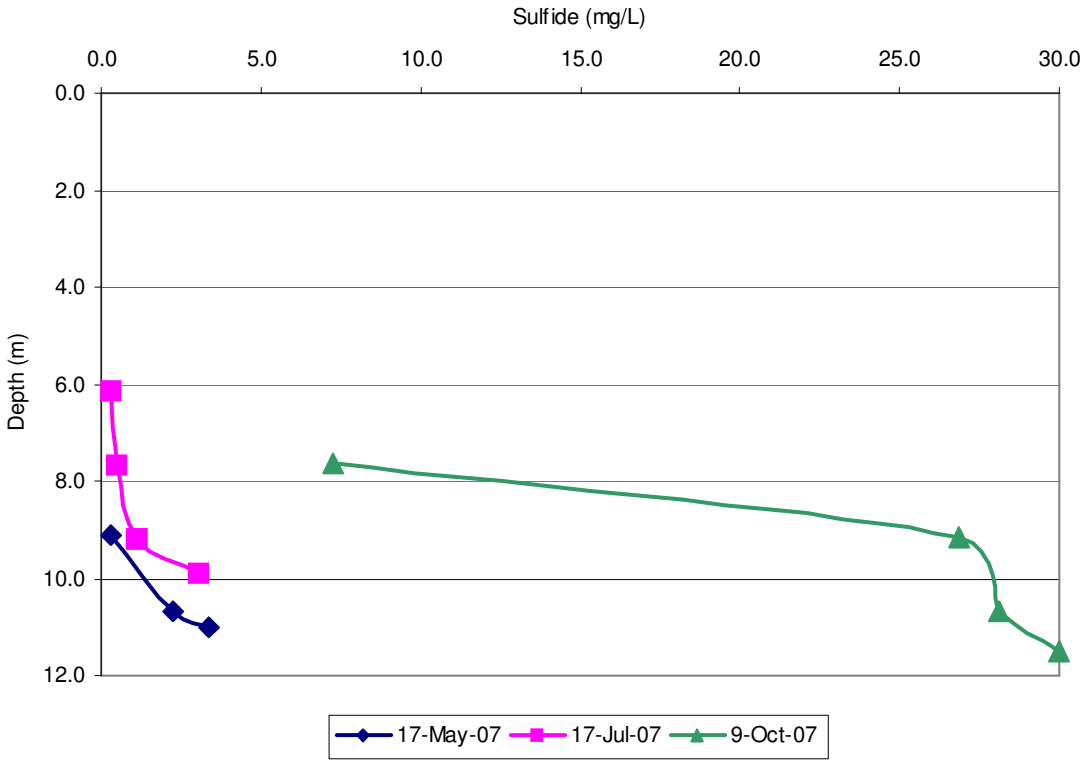

Figure 9- Sulfide concentrations with depth over time

Ammonium, a product of the anaerobic reduction of nitrate, was also detected in the hypolimnion of Crystal Lake. The overall values of ammonium increase with depth and over time (Fig. 10). Ammonium increases with depth from an increase of decomposition in the hypolimnion. Decomposition over time causes ammonium to build up in the hypolimnion, resulting in the increase of ammonium over time.

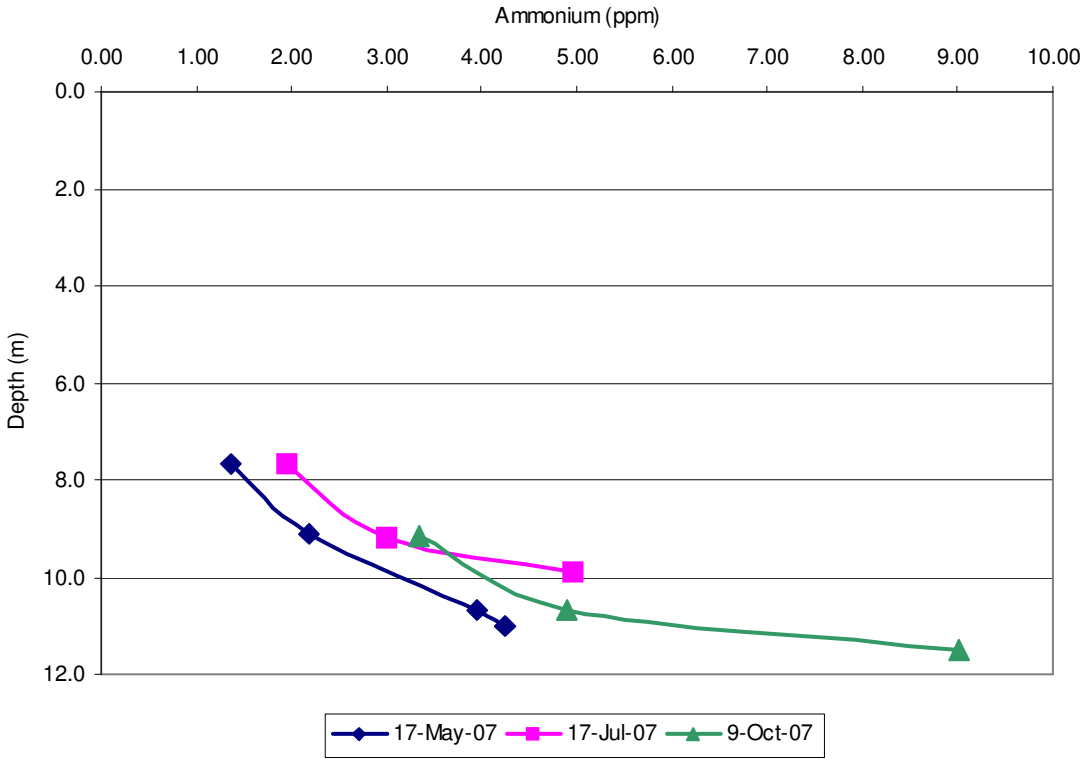

Figure 10- Ammonium concentrations with depth over time

The calcium concentration in the epilimnion and metalimnion generally decreases over time (Fig. 11). The precipitation of calcium carbonate, caused by the increased pH values from photosynthesis, causes this decrease. In contrast, the calcium concentration increases in the hypolimnion, due to the dissolution of calcium carbonate from low pH values.

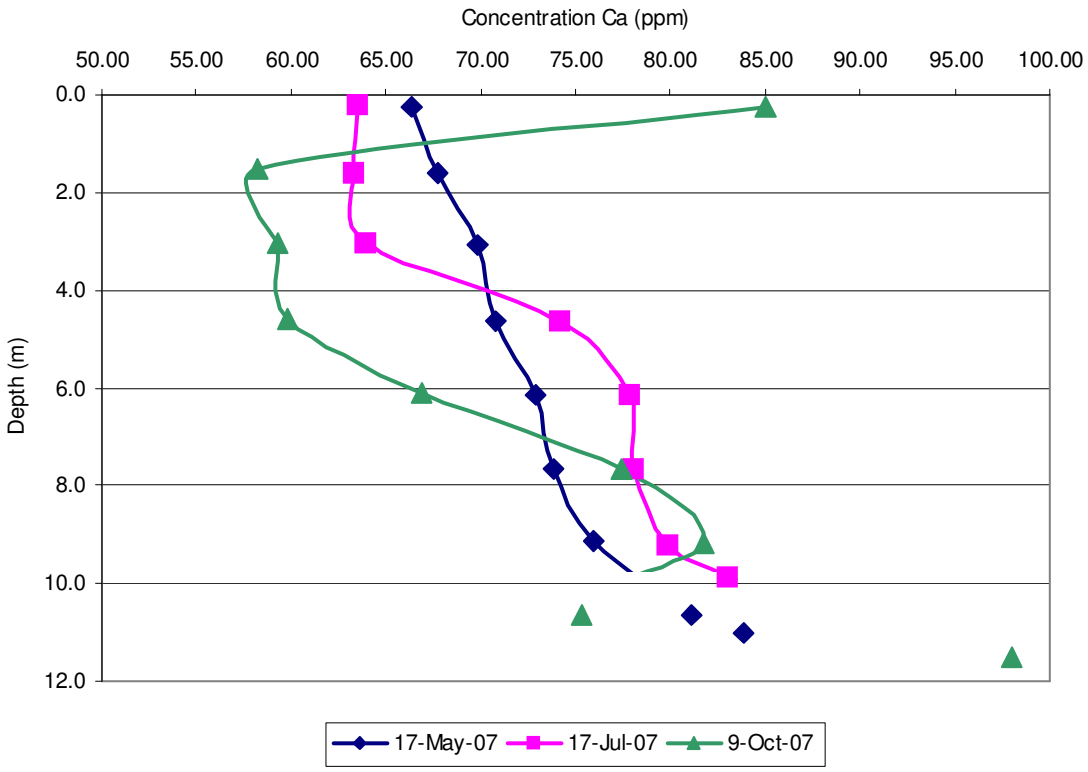

Figure 11- Calcium concentrations with depth over time

Potassium (Fig. 12), magnesium (Fig. 13), and sodium (Fig. 14) concentrations are fairly consistent, but all increase with depth and time. The increase in depth is from the decomposition of biomass in the hypolimnion, releasing nutrients back into the water column. While used only in small quantities, these three ions are used to regulate ion balances; fluctuations of these ions in the epilimnion and metalimnion may be caused by changes of intracellular ion concentrations.

Another possible cause of the trends seen in these three nutrients is dilution. Potassium, magnesium, and sodium concentrations are much lower in May than at any other time. Increased runoff from snowmelt in early spring may have contributed to the lower concentrations of these nutrients. The constant magnesium concentration over time also indicates that magnesium is not precipitating with carbonate.

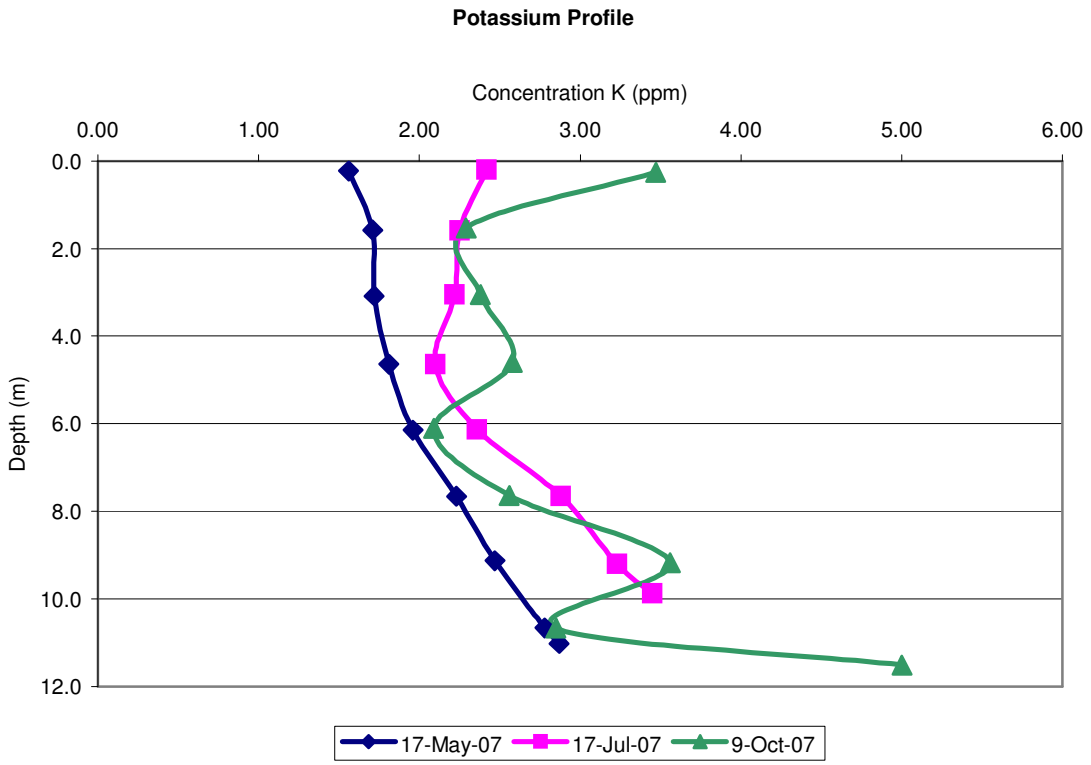

Figure 12- Potassium concentrations with depth over time

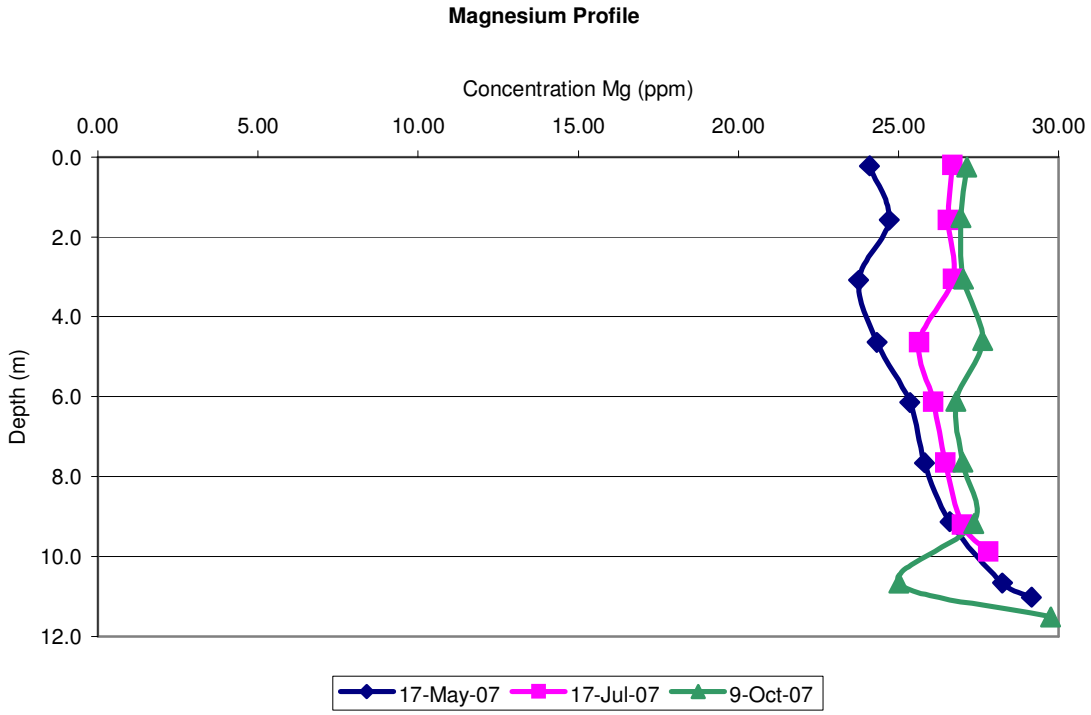

Figure 13- Magnesium concentrations with depth over time

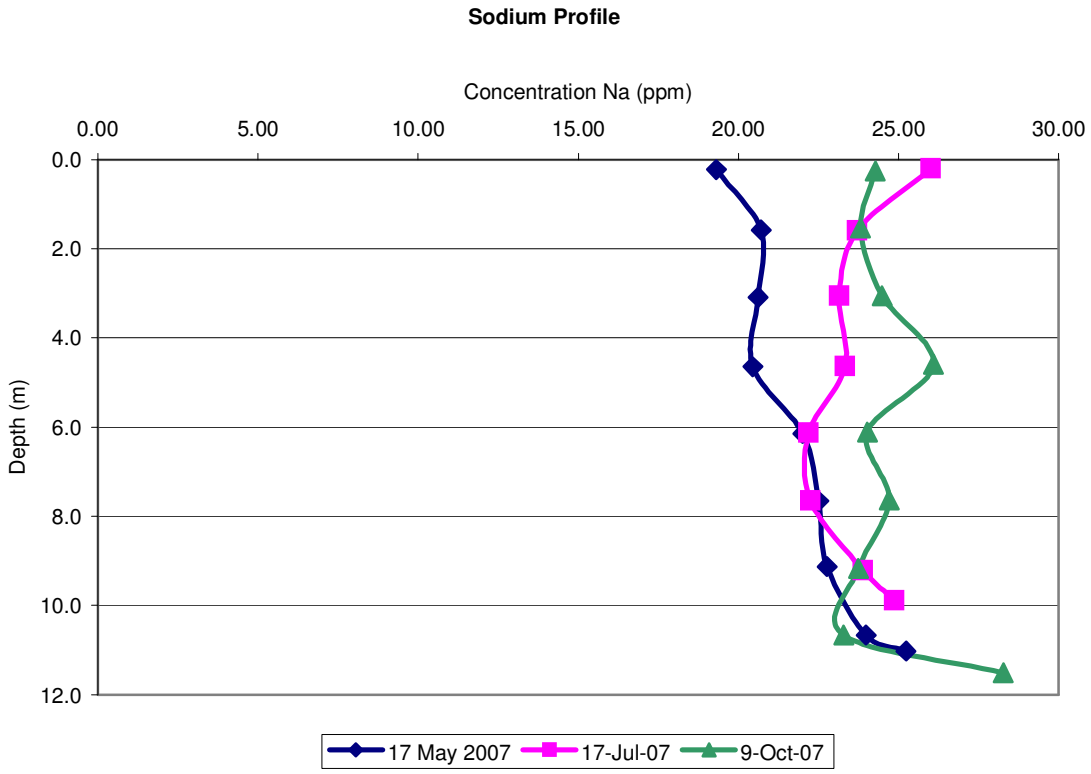

Figure 14- Sodium concentrations with depth over time

Silica concentrations increase over time in Crystal Lake (Fig. 15). This indicates an outside source of silica, likely from the glacial till in the area. Silica values are lower in the epilimnion and metalimnion from the uptake by diatoms for cell wall growth. Concentrations then increase in the hypolimnion from the decomposition of diatoms, releasing silica back into the water column. This increase may also be caused by the sediments of the lake bottom, which are likely rich in allumino-silicate minerals.

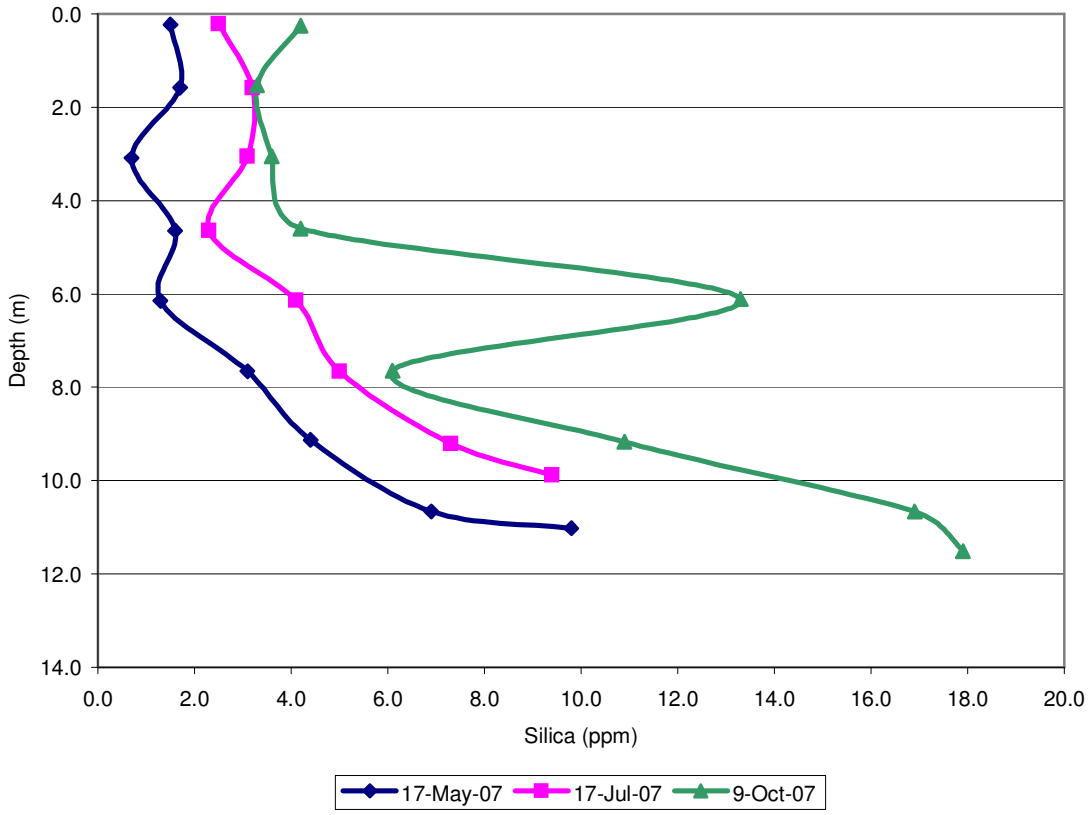

Figure 15- Silica concentrations with depth over time

Phosphate levels in the epilimnion and metalimnion decrease slightly over time (Fig. 16). The amount of phosphate rapidly increases in the hypolimnion, caused by the release of phosphate during decomposition.

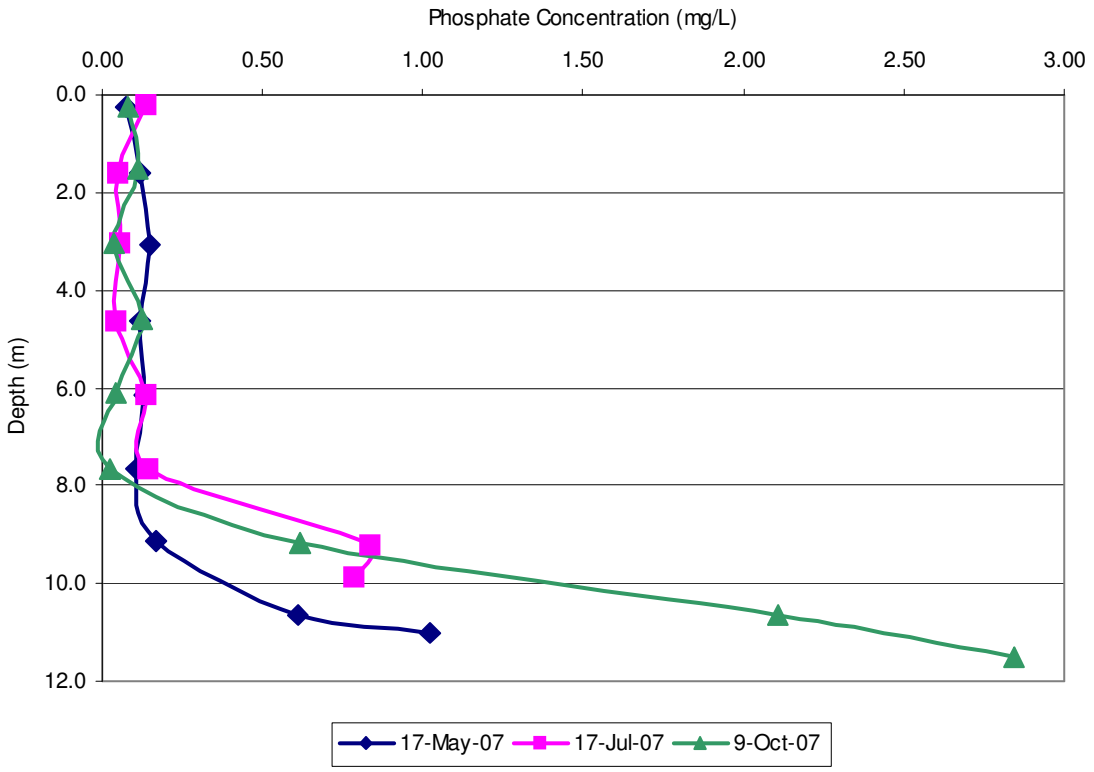

Figure 16- Phosphate concentration with depth over time

Since phosphate is used by algae, it was expected that phosphate concentrations would be low in areas where algae were photosynthesizing. There are two distinct relationships seen (Fig. 17): one for the oxic zone (the epilimnion and metalimnion) and one for the anoxic zone (hypolimnion). In the oxic zone, the phosphate concentration is relatively constant, ranging from .037 to .175 mg/L. In the anoxic zone, phosphate concentrations increase as the dissolved oxygen decreases. Phosphate is being released in the anoxic zone from the decomposition of algae.

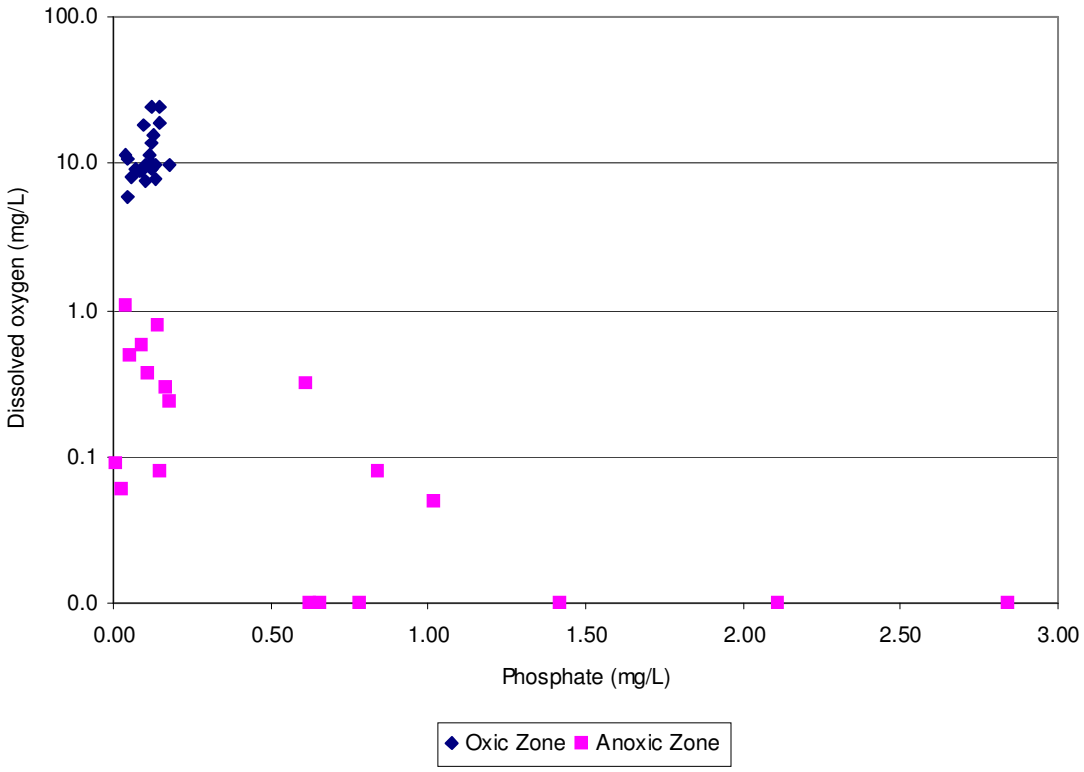

Figure 17- Phosphate versus dissolved oxygen

Nitrate is also an important nutrient for algal growth. Nitrate concentrations are at a low, constant value in the epilimnion and metalimnion (Fig. 18). The unexpected high value in the hypolimnion in the July sample is most likely due to contamination of the sample bottle.

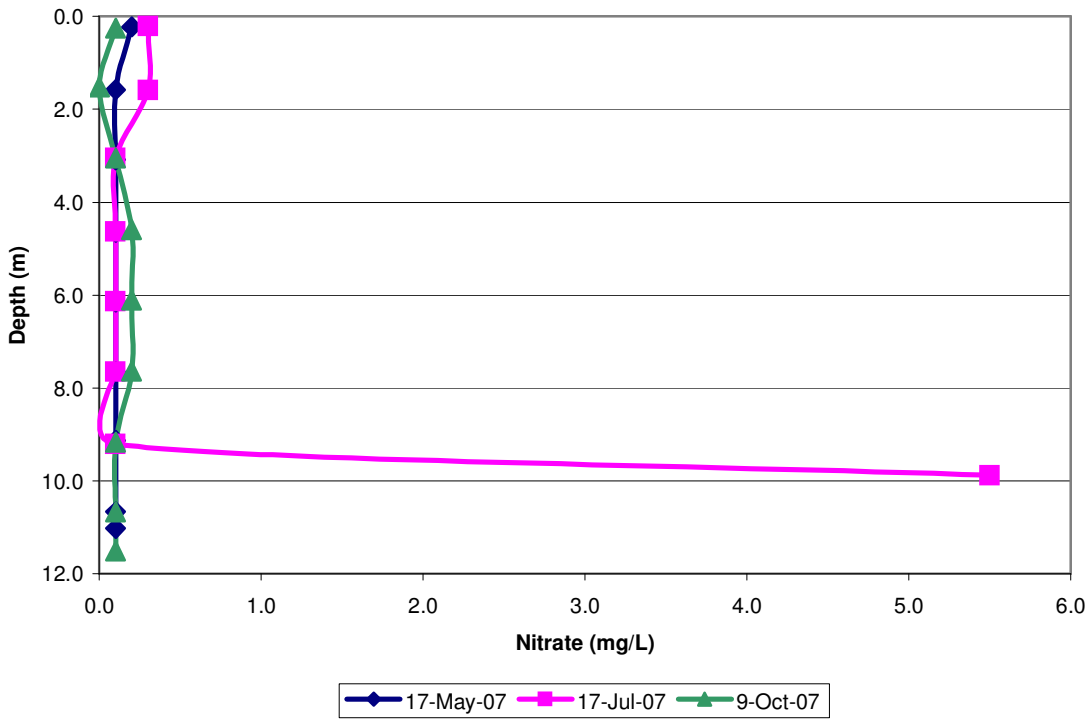

Figure 18- Nitrate Concentrations with depth over time

4.3 Chlorophyll and algae analysis

The relative concentrations of chlorophyll types detected during analysis were used to determine the most common algal members at various times and depths in Crystal Lake. Chlorophyll a, which indicates total biomass, is by far the greatest in May (Fig. 19). Concentrations decrease between May and October, and start to rise again in October. Chlorophyll b follows the same pattern as chlorophyll a, indicating that green algae are a significant contributor to total biomass in Crystal Lake, with a bloom in May and possibly another forming in October. However, the significantly higher amount of chlorophyll a in May suggests a bloom in cyanobacteria as well.

Chlorophyll c has a different trend than chlorophyll a or chlorophyll b. The highest measured chlorophyll c is seen in June. Concentrations then decrease between June

and October, and start to rise in mid-October. This indicates a diatom bloom in June, and possibly another in mid-late October.

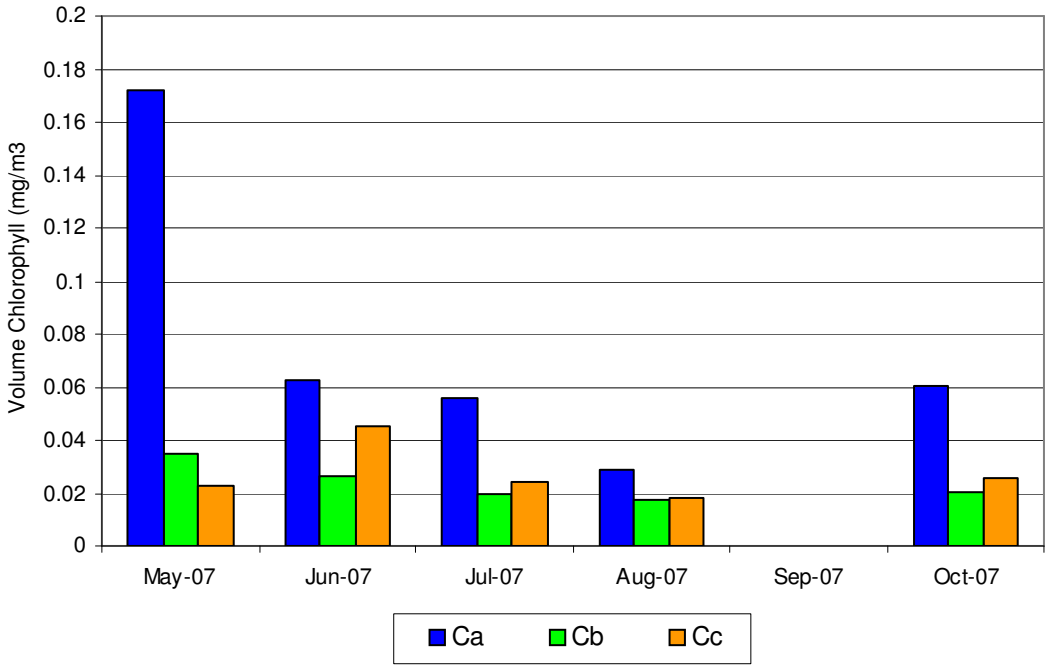

Figure 19- Total chlorophyll over time

The total amount of biomass in Crystal Lake was calculated from chlorophyll a analysis (Fig. 20). There is a marked peak in biomass in the metalimnion on all sample dates. The greatest biomass peak is seen in May; the biomass peaks are roughly the same concentration in July and October. These peaks are at slightly different depths, which is a result of the vertical migration of algae through the water column. There are also variations in nutrient availability over the seasons, which would lead to peak algae concentrations at different depths.

Biomass increases at bottom depths in both May and July. However, this is simply a relic of the settling of biomass over time. This trend does not occur in October because of the high rates of decomposition occurring, as indicated by the high sulfide concentrations at this time (Fig. 9).

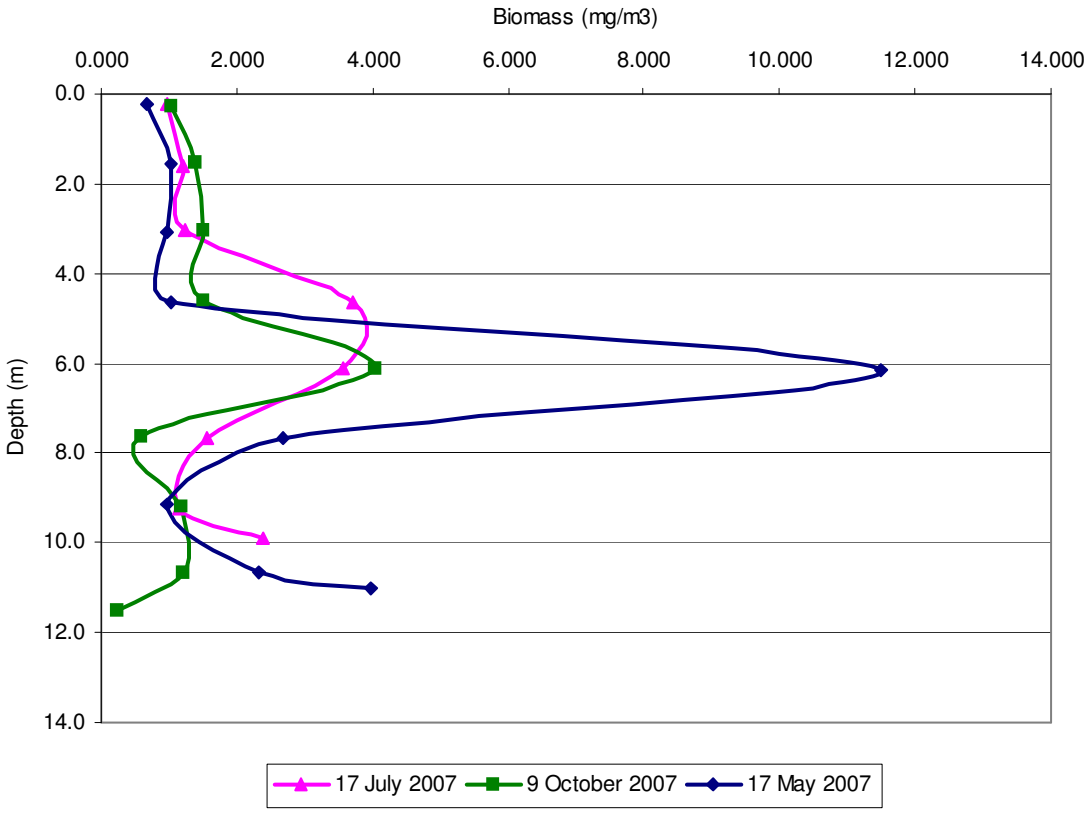

Figure 20- Biomass with depth

As discussed in Section 4.1, there are two possibilities for the dissolved oxygen concentrations in the epilimnion (Fig. 9): either from photosynthesis followed by atmospheric equilibration, or only by equilibration. Based on the biomass profile, there is little photosynthesis in the epilimnion. This suggests that lower dissolved oxygen in the epilimnion is due to lower photosynthesis, and that concentrations are in equilibrium with the atmosphere.

The variations of chlorophyll types and dissolved oxygen over the sample period are shown below. In May, the dissolved oxygen peaks below 5 meters; chlorophyll b and chlorophyll c peak just above 8 meters (Fig. 21), at the base of the oxic zone. Chlorophyll increases again in the hypolimnion from the settling of algae. At the bottom of the lake, chlorophyll b and chlorophyll c decrease from decomposition. Chlorophyll a does not yet seem affected by decomposition. Chlorophyll b is much more prevalent than chlorophyll c at this time, indicating that green algae are the dominant algal member in May.

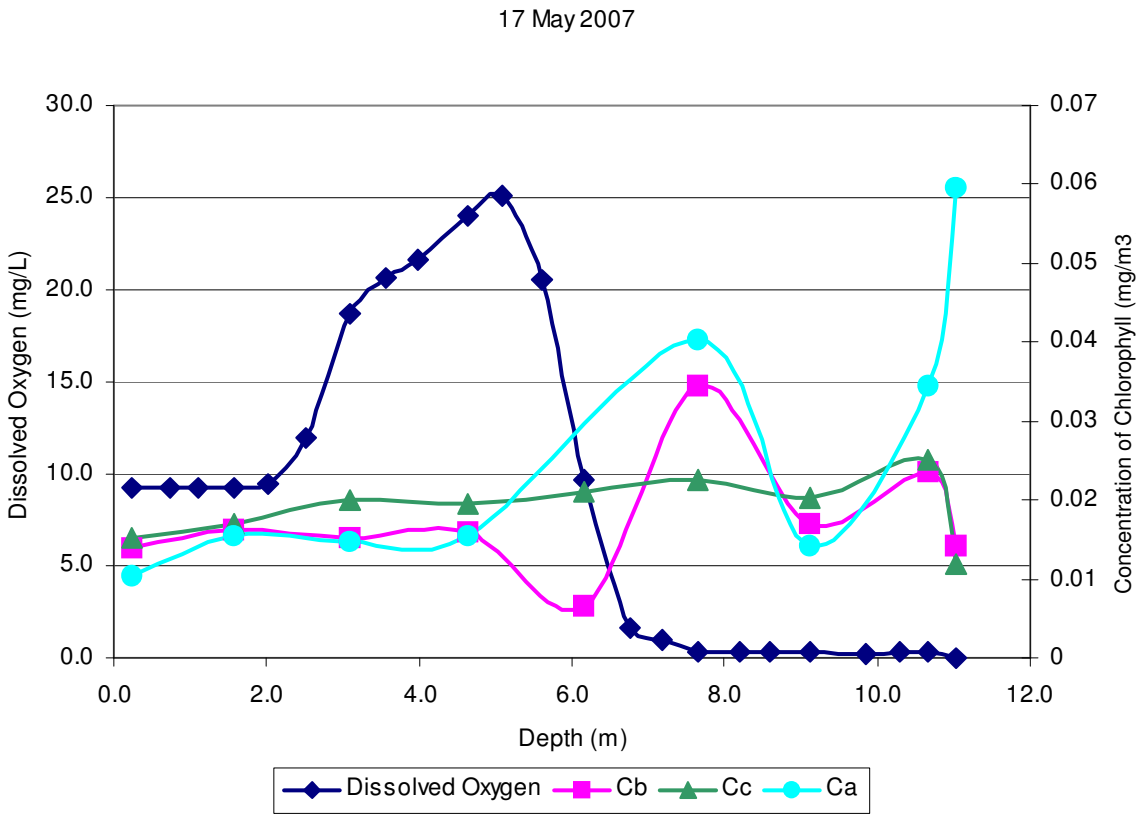

Figure 21- Chlorophyll types versus dissolved oxygen- 17 May 2007

In July, chlorophyll a peaks near 5.5 meters, chlorophyll b peaks near 3 meters, chlorophyll c peaks near 5 meters, and dissolved oxygen peaks around 4.5 meters (Fig. 22). Chlorophyll a follows the same general pattern as dissolved oxygen. However, there is a slight lag between these two variables, indicating the migration of the biomass. The amount of chlorophyll c is much greater than chlorophyll b in July, indicating that diatoms are now the more dominant member in the algal community at this time. The pattern of chlorophyll b and chlorophyll c are opposite, indicating possible competition between green algae and diatoms. In the hypolimnion, chlorophyll a and chlorophyll b decrease steadily, and then increase from settling. Chlorophyll c begins to increase at the lake bottom, but then decreases sharply from decomposition. It is unclear why green algae do not appear to be decomposing at this time.

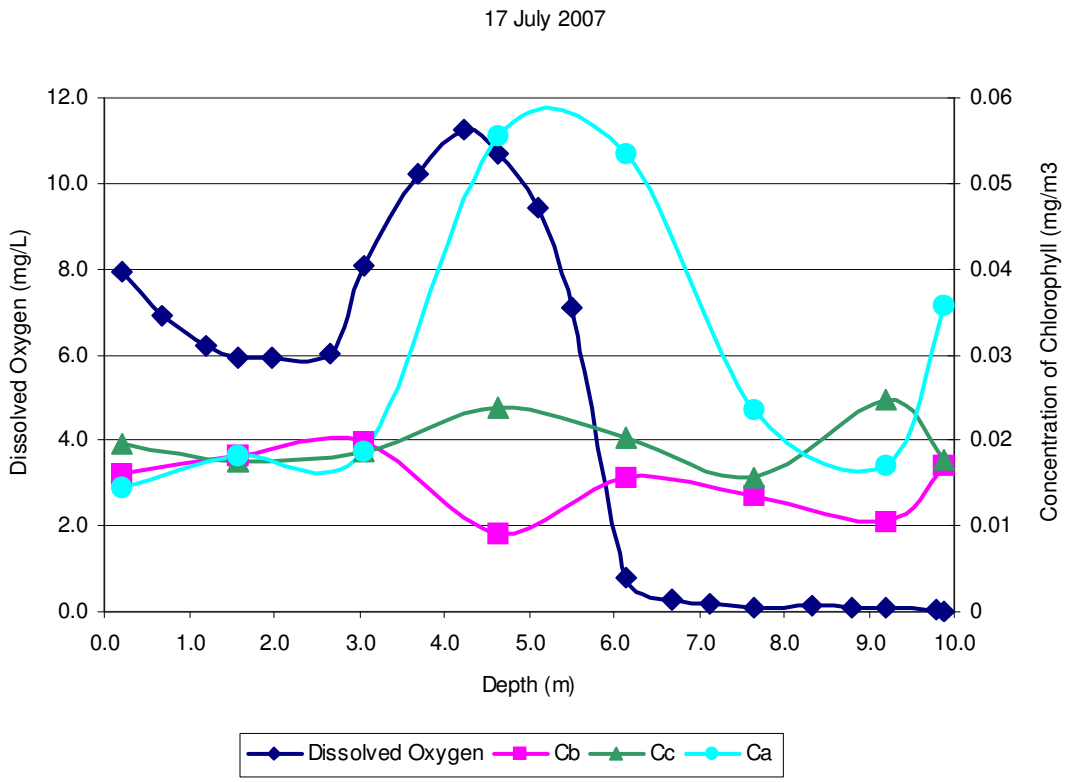

Figure 22- Chlorophyll types versus dissolved oxygen- 17 July 2007

In October, chlorophyll a, chlorophyll b, and chlorophyll c have the same pattern; all peak near 2.5 meters, decrease in the metalimnion, and increase again just above the hypolimnion (Fig. 23). In the hypolimnion, there is another peak due to settling, and then decomposition causes a sharp decline at the lake bottom. Chlorophyll c is greater than chlorophyll b, indicating that diatoms are more prevalent than green algae. The peak in dissolved oxygen occurs below 4.5 meters, when all chlorophyll types are low in concentration. This is likely an artifact of the vertical migration of algae. A majority of photosynthesis occurred near 4.5 meters; the algae then migrated lower in the water column, leaving the relic of their activity behind.

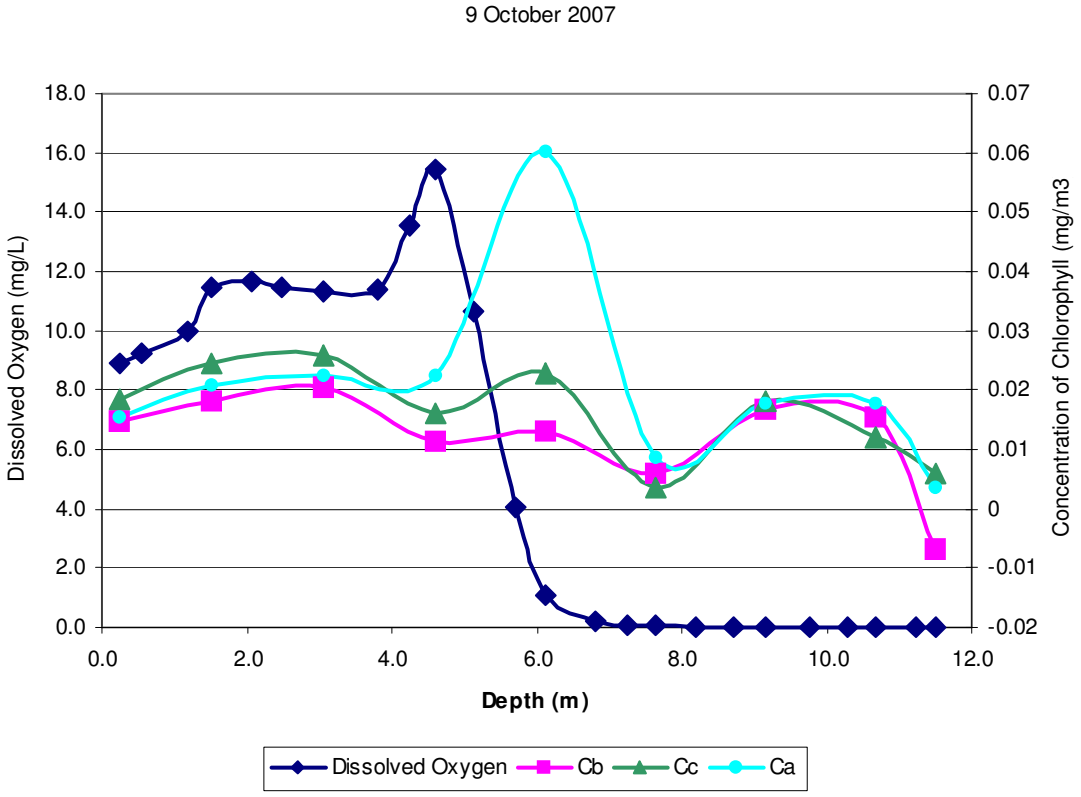

Figure 23- Chlorophyll types versus dissolved oxygen- 9 October 2007

The apparent peak blooms of diatoms, green algae, and dissolved oxygen occur at different times. It was expected that these values would coincide since they are so closely linked. The differences observed in the data illustrate the vertical migration of algae through the water column. Algae photosynthesize at levels with optimum nutrients, light, and carbon dioxide; once these parameters become unfavorable, they move to different depths of the lake. However, they leave their photosynthetic signature- high dissolved oxygen and high pH- behind.

4.4 Carbon isotope analysis

Sample dates for carbon isotope analysis were reduced to those where the best overall data was collected. These dates were 17 May, 17 July, and 9 October 2007. The results of analysis are shown in Appendix D.

Overall, $\delta^{13}C$ values are higher in the epilimnion and metalimnion (Fig. 24), where photosynthesis occurs. The peak $\delta^{13}C$ values are at similar depths in May and July, but the peak is more shallow in October. This indicates that the depth of photosynthesis changes through the seasons. The peak of $\delta^{13}C$ in July is unexpectedly lower than in May; in July, the pH of the epilimnion is higher, causing calcium carbonate to precipitate and lowering the $\delta^{13}C$ in the epilimnion. There is also less photosynthesis occurring in July, as seen from chlorophyll analysis.

The $\delta^{13}C$ values decrease in the hypolimnion; algae, which are isotopically light with regard to carbon isotopes, decompose in the hypolimnion, releasing carbon of lighter isotope composition into the water column and decreasing the $\delta^{13}C$.

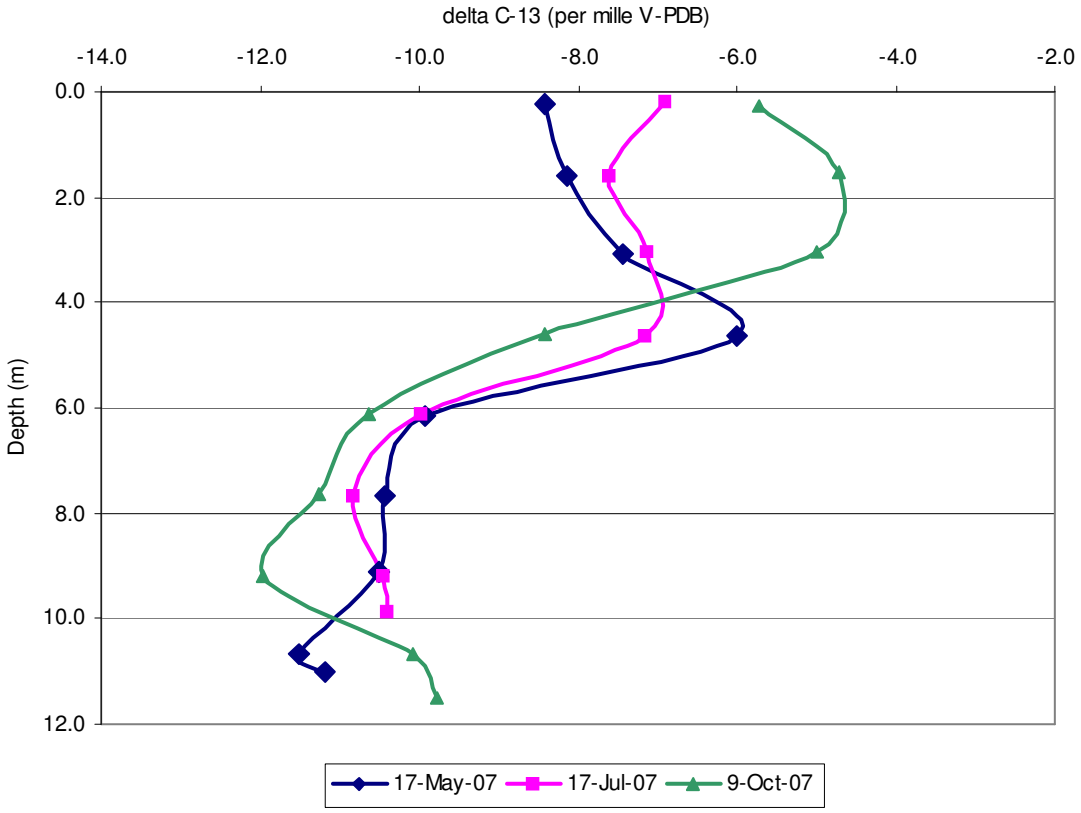

Figure 24- $\delta^{13}C$ with depth over time

Photosynthesis is known to have a significant effect on the fractionation of carbon. Therefore, a cross plot of $\delta^{13}C$ and the concentration of chlorophyll was created (Fig. 25). There is an overall increase in $\delta^{13}C$ as the concentration of chlorophyll increases, despite a weak correlation.

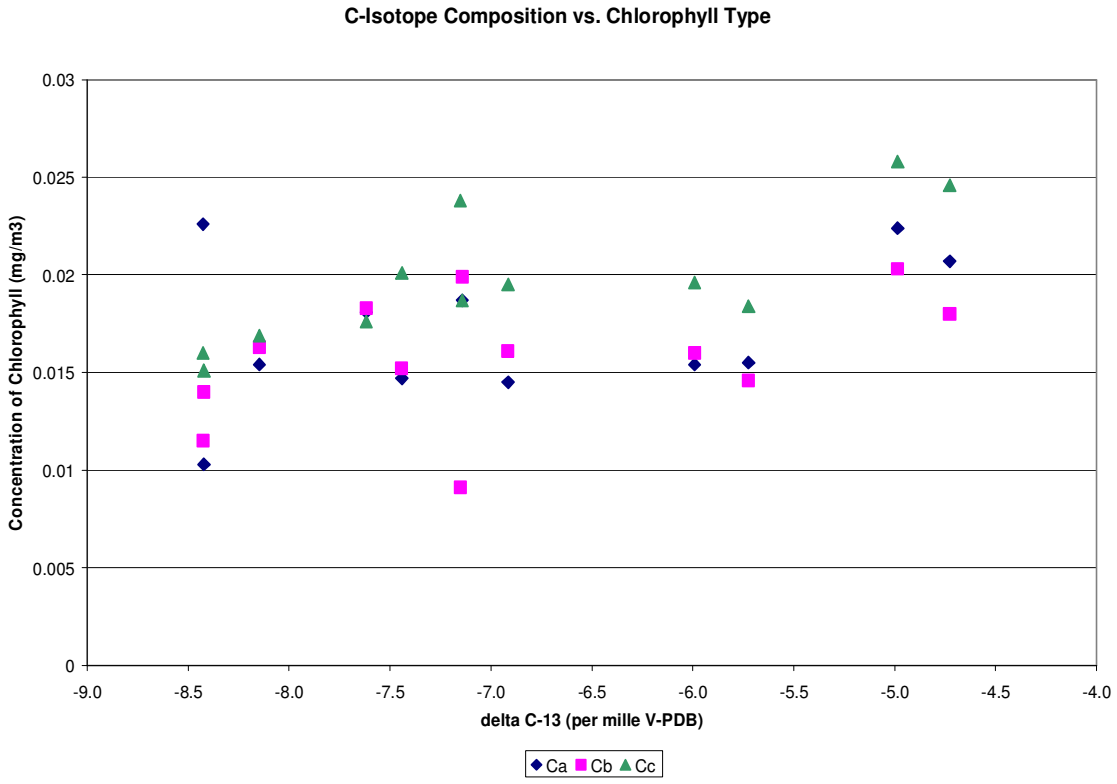

Figure 25- $\delta^{13}C$ values versus chlorophyll type

As discussed in Section 4.3, algae tend to migrate through the water column. Therefore, the effect of photosynthesis is not always seen in the same areas that algae are detected. Dissolved oxygen and pH are better indicators of photosynthesis, as are the concentrations of essential nutrients. For that reason, cross plots were constructed to compare these indicators to $\delta^{13}C$ measurements.

The trend observed between $\delta^{13}C$ and dissolved oxygen is as expected; as dissolved oxygen increases from photosynthesis, $\delta^{13}C$ becomes more positive (Fig. 26). This trend is seen for each individual sample day, as well as over the time period of this study. Algae prefer to use ^{12}C for photosynthesis, leaving the residual water enriched in ^{13}C. There is a cluster of values where the dissolved oxygen is nearly zero; in this area, the $\delta^{13}C$ values are much more negative. The area of low dissolved oxygen is in the

hypolimnion, where isotopically light algae decompose, releasing isotopically-light carbon back into the water column and decreasing the $\delta^{13}C$.

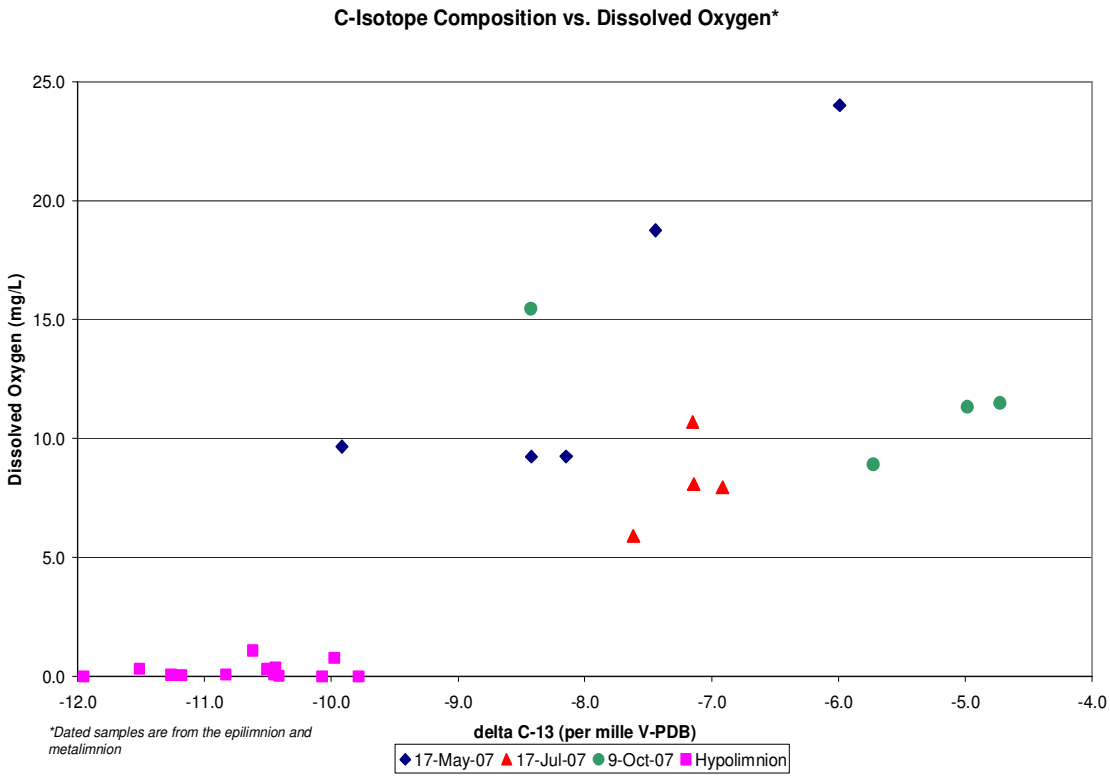

Figure 26- Dissolved oxygen versus $\delta^{13}C$ values

There is also a trend seen when comparing dissolved oxygen and $\delta^{13}C$ based on the different strata within Crystal Lake (Fig. 27). As mentioned, samples from the hypolimnion have low $\delta^{13}C$ values and dissolved oxygen concentrations. Samples from the metalimnion have greater concentrations of dissolved oxygen than samples from the epilimnion. This is because a majority of photosynthesis occurs in the metalimnion. The semi-closed environment in the metalimnion also better preserves the effect of photosynthesis on the $\delta^{13}C$ of dissolved inorganic carbon. The range of $\delta^{13}C$ values are about the same for both the epilimnion and metalimnion.

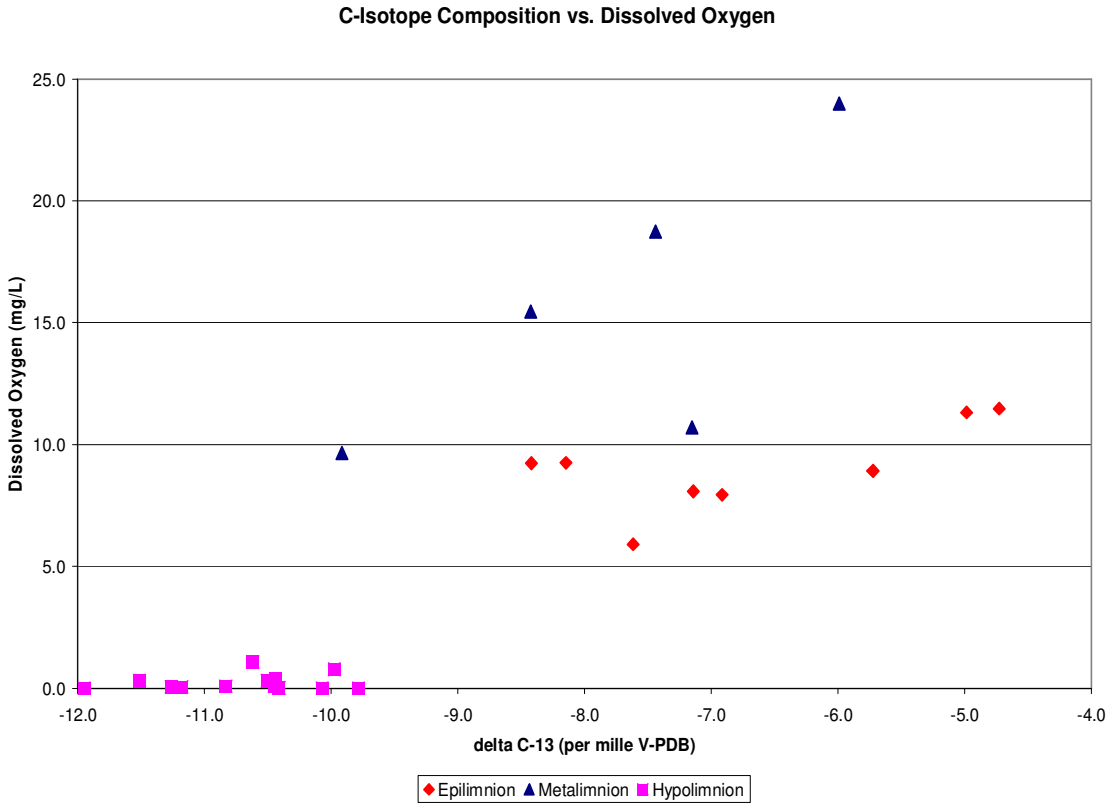

Figure 27- Dissolved oxygen versus $\delta^{13}C$ values based on limnological strata

In general, similar trends are seen when comparing pH with $\delta^{13}C$ measurements (Figs. 28 and 29). As the pH increases from the consumption of carbon dioxide during photosynthesis, $\delta^{13}C$ increases. The pH decreases in the hypolimnion, where decomposition occurs and isotopically-light carbon enters the water column, decreasing $\delta^{13}C$. However, pH values vary over time, with the highest pH values in July. The pH also varies within limnological strata; the highest pH values and highest $\delta^{13}C$ values are seen in the epilimnion. However, this cluster of sample points is from October, when the depth of the metalimnion is much greater and most photosynthesis occurs in the epilimnion.

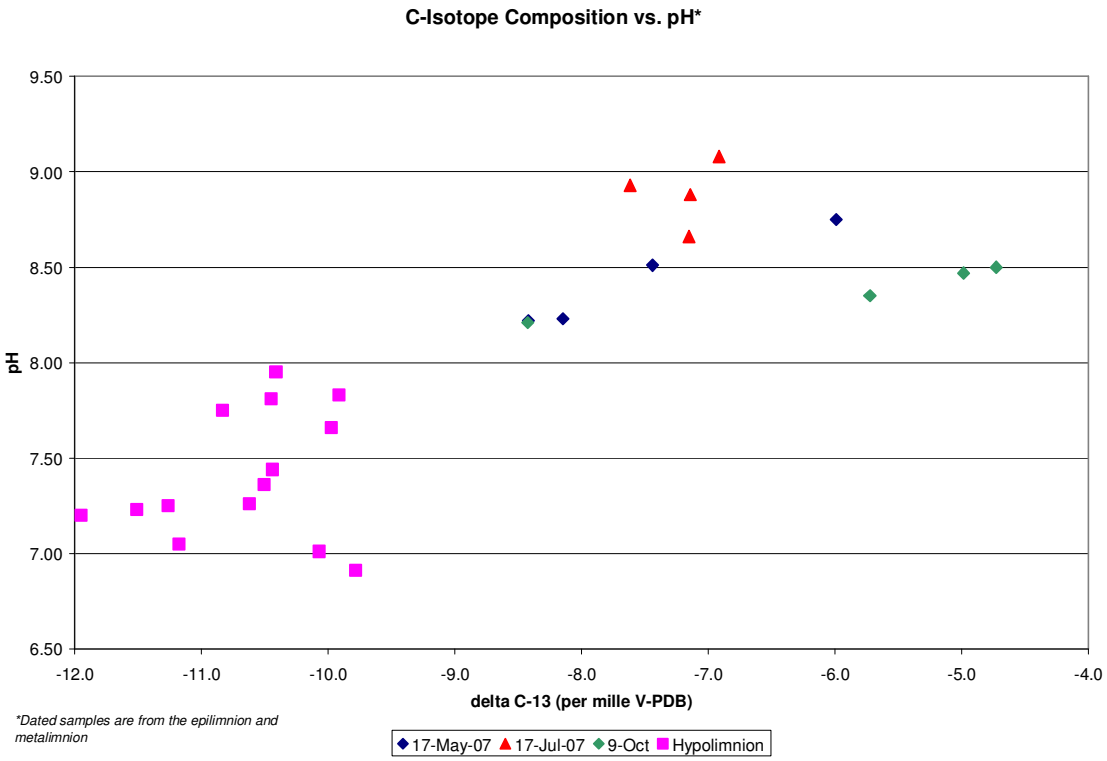

Figure 28- pH versus $\delta^{13}C$ values

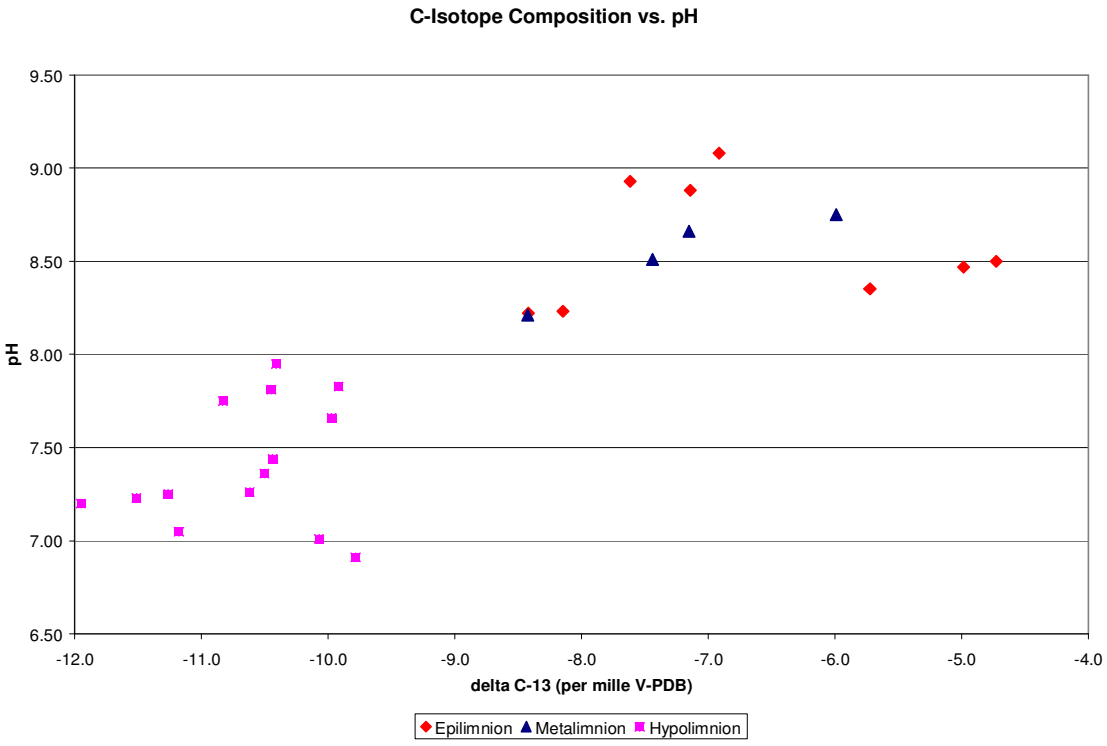

Figure 29- pH versus $\delta^{13}C$ values based on limnological strata

The trends observed when comparing $\delta^{13}C$ with several nutrients important to algae also indicate that the presence of algae has an effect on carbon isotope fractionation. All $\delta^{13}C$ values at and below -9.8 ‰ V-PDB are from samples in the hypolimnion, and are excluded from the data below.

Both phosphate (Fig. 30) and calcium (Fig. 31) generally decrease over time while $\delta^{13}C$ values increase over time. Phosphate is a major nutrient consumed by algae, and calcium is used by green algae to build cell walls, causing the nutrient concentrations to gradually decrease. Photosynthesis over time causes the $\delta^{13}C$ values to increase. The dissolution and precipitation of calcite may also contribute to the trends observed in calcium values.

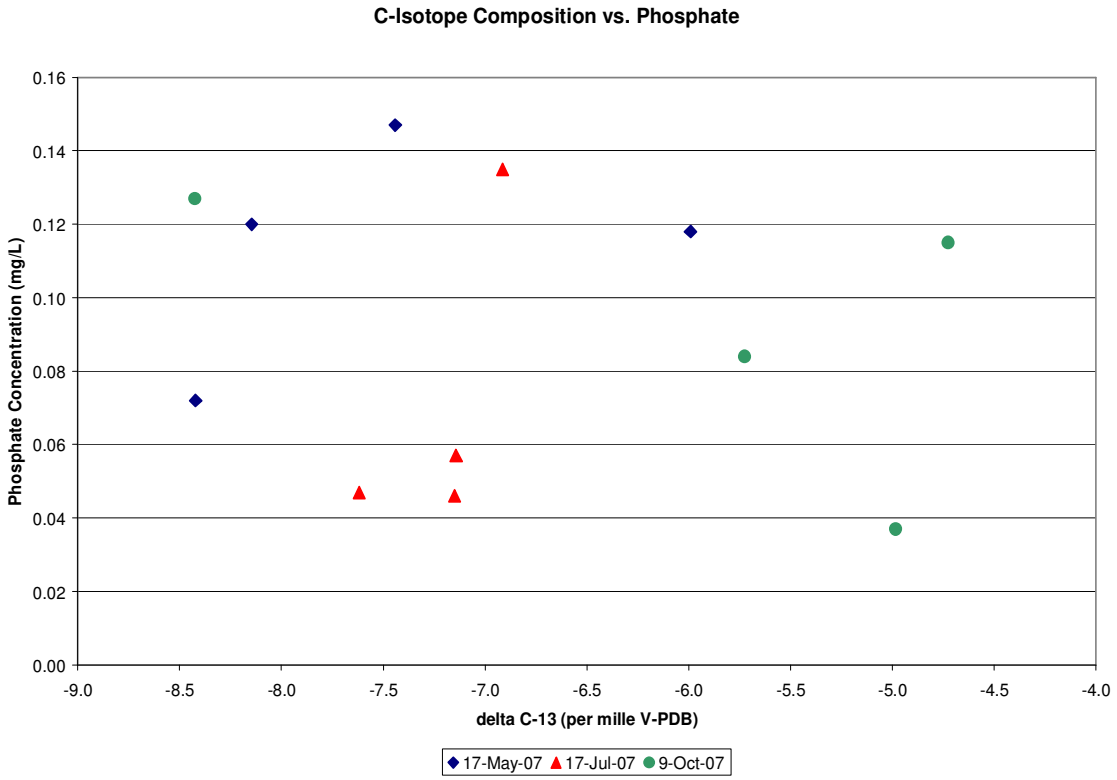

Figure 30- Phosphate versus $\delta^{13}C$ values

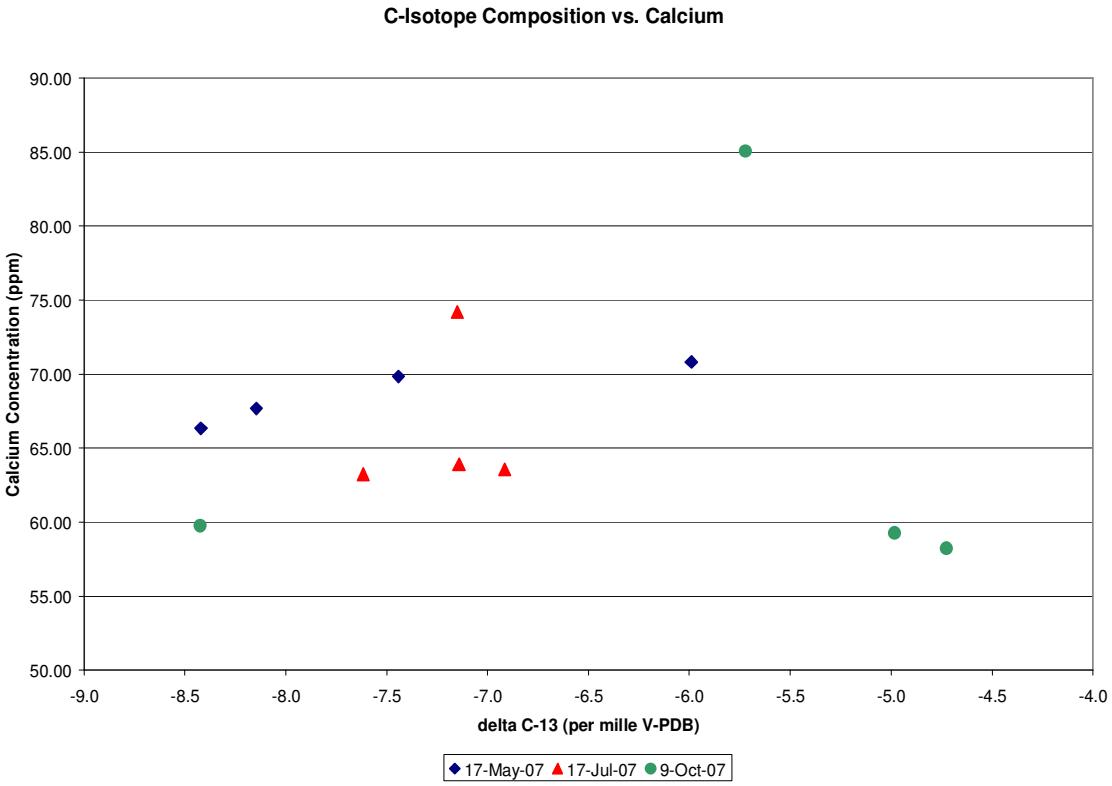

Figure 31- Calcium versus $\delta^{13}C$ values

The opposite trend is observed when comparing sodium (Fig. 32), potassium (Fig. 33), magnesium (Fig. 34), and silica (Fig. 35) concentrations with $\delta^{13}C$ values. These nutrients increase over time. Sodium, potassium, and magnesium are used in small amounts by algae for intracellular ion balance, while silica is used by diatoms to build cell walls. Photosynthesis can cause differences in these concentration gradients, and may have resulted in algae releasing these nutrients to restore equilibrium. However, as discussed, other factors may have resulted in the trends observed in these nutrients. Silica values increase over time due to the decomposition of diatoms, as well as the influx of silica from sediments.

It is interesting to note that silica and magnesium concentrations decrease on each sample date as $\delta^{13}C$ values increase. These nutrients appear to be consumed by algae; despite this, their concentrations somehow increase over time. It is possible that silica and magnesium could have entered Crystal Lake from soil runoff or calcite dissolution.

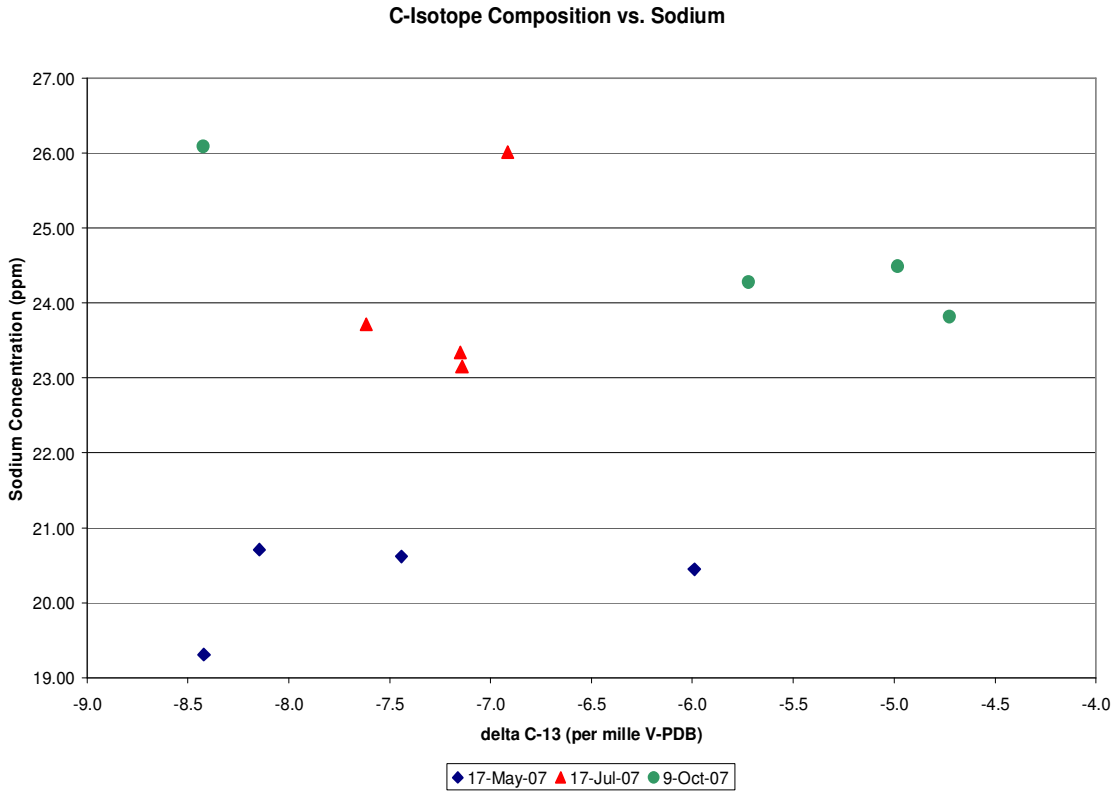

Figure 32- Sodium versus $\delta^{13}C$ values

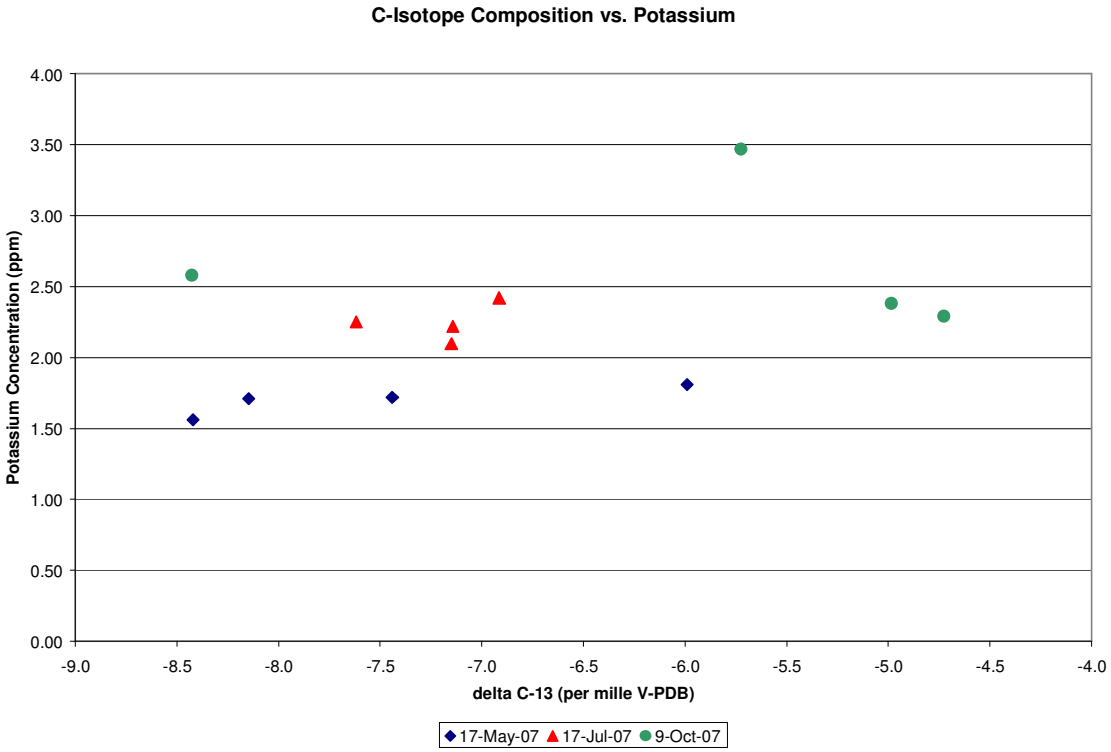

Figure 33- Potassium versus $\delta^{13}C$ values

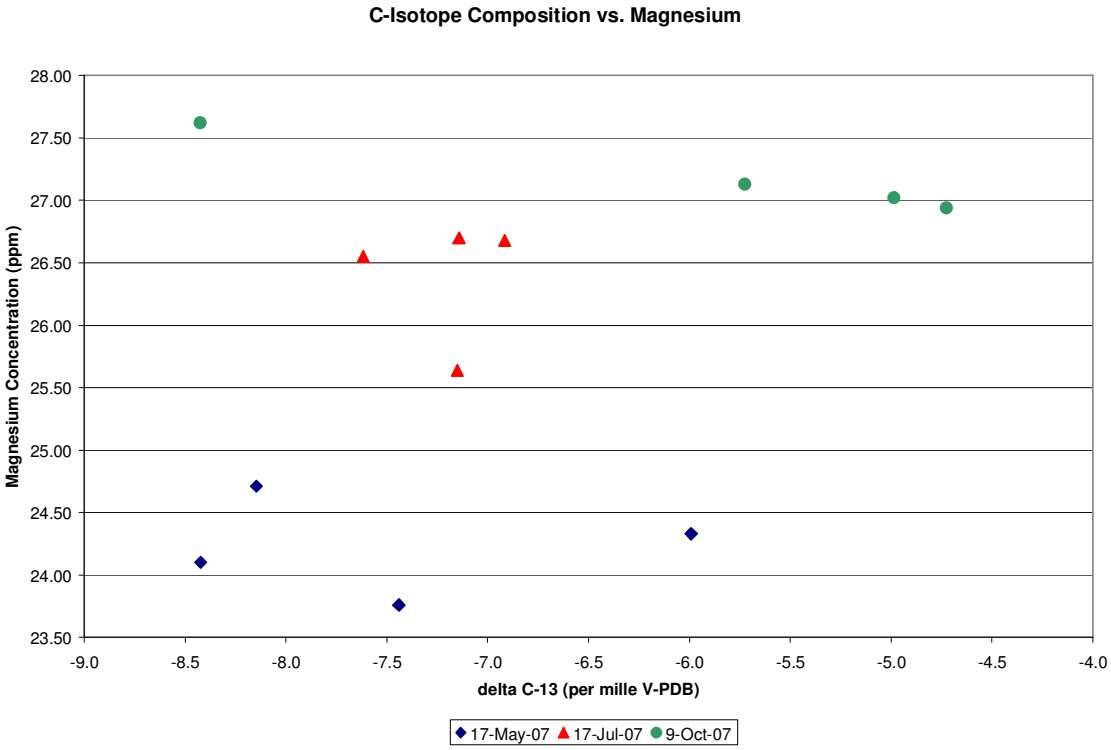

Figure 34- Magnesium versus $\delta^{13}C$ values

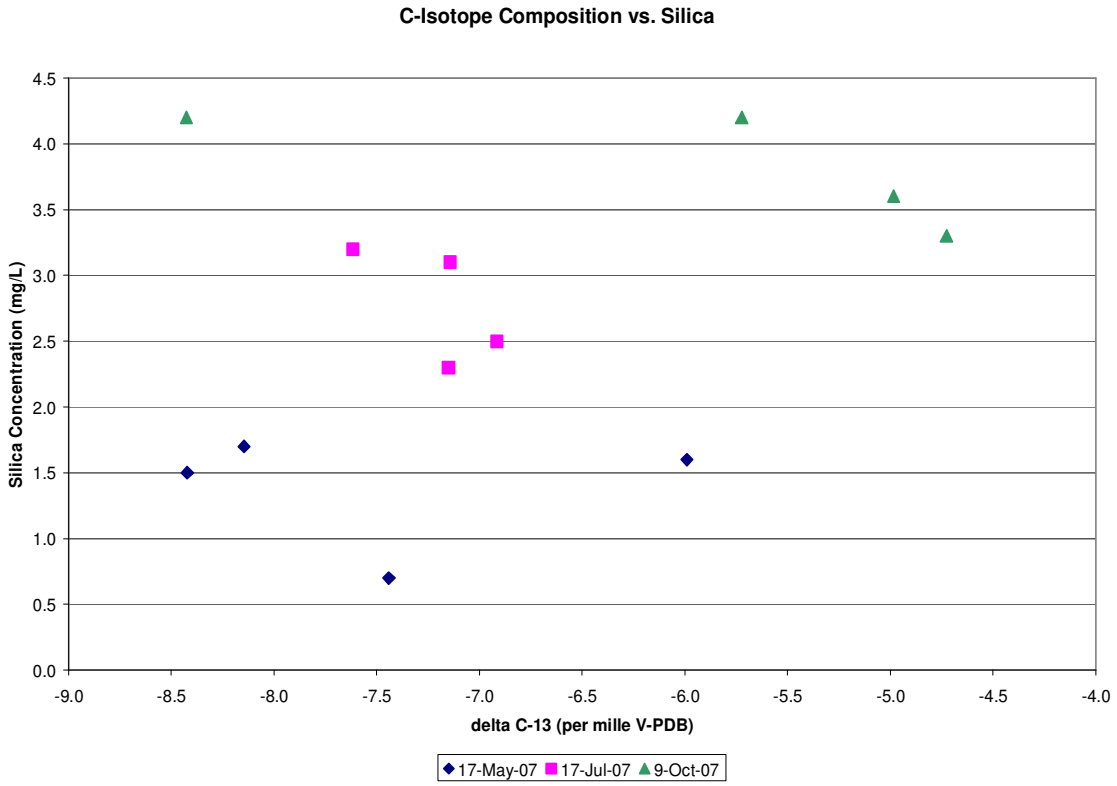

Figure 35- Silica versus $\delta^{13}C$ values

Chlorophyll analysis indicates that green algae, and possibly cyanobacteria, are the dominant members of the algal community in May. However, after the diatom bloom in June, diatoms become the dominant member of the algal community in Crystal Lake, and remain so through October. Dissolved oxygen and chlorophyll a follow the same general trend on all sample days (Figs. 20, 21, and 22), which was expected since chlorophyll a is a direct measure of the amount of biomass; when there is more biomass, photosynthesis increases, which increased the amount of dissolved oxygen in the water column. The pH values also increase in areas of photosynthetic activity.

Several micronutrients measured have some interesting trends in Crystal Lake. Phosphate and calcium concentrations decrease over time from algal consumption; magnesium, silica, sodium, and potassium increase over time, due to algal ion regulations, decomposition, and sediment influx.

Values of $\delta^{13}C$ in Crystal Lake vary with depth and over time, due to differences in photosynthetic activity and decomposition. Algae preferentially use ^{12}C as a carbon source during photosynthesis, increasing $\delta^{13}C$; when the isotopically-light algae decompose in the hypolimnion, decreasing $\delta^{13}C$.

When the $\delta^{13}C$ values were compared to several other measurements from Crystal Lake, several trends became apparent. The strongest trends are with parameters of photosynthesis, such as dissolved oxygen and pH, although several trends are seen between $\delta^{13}C$ and nutrients as well. These trends are listed below.

- $\delta^{13}C < -10$ V-PDB:
    - Sample is from the hypolimnion
    - pH is below 8
    - Dissolved oxygen is between 0-1 mg/L
- $-9 < \delta^{13}C < -6$ V-PDB:
    - Sample is from the epilimnion or metalimnion
    - pH is > 8
    - Dissolved oxygen is between 5-20 mg/L
    - Calcium is above 60 ppm
    - Magnesium is below 27 ppm
    - Silica is below 3.25 mg/L

- $\delta^{13}C$ > -6 V-PDB:
    - Sample is from the epilimnion
    - pH is between 8-9
    - Dissolved oxygen is between 10-30 mg/L
    - Calcium is below 60 ppm
    - Magnesium is greater than 27 ppm
    - Silica is above 3.25 mg/L
    - Sodium is between 24-25 ppm

Although interesting, these results are based on a single study conducted at one site over one season. More research in this area of hydrogeochemistry will help to validate these trends. Studies should be conducted over longer periods and at multiple sites to help establish the impact of nutrient concentrations on carbon isotope fractionation.

5.0 Conclusions

Crystal Lake is a thermally-stratified, eutrophic kettle lake. Few lakes follow the definitions of these parameters as closely as Crystal Lake, making it a prime location for limnological studies. Decomposition occurs in the hypolimnion, indicated by the lack of dissolved oxygen, the presence of ammonium, and the presence of sulfide.

Through chlorophyll analysis, it was inferred that the Crystal Lake contains substantial amounts of green algae and diatoms, as well as cyanobacteria. The amounts and distributions of these phytoplankton communities vary over time, with green algal blooms in the spring and fall, and a diatom bloom in the summer. Diatoms are the dominant member of the phytoplankton community from June through October.

Photosynthesis is the major process that fractionates carbon isotopes. This was determined by comparing $\delta^{13}C$ values with dissolved oxygen, pH, and nutrients. Fractionation occurs in the photic zones, where photosynthesis takes place; the continuing photosynthesis over time causes a gradual increase in $\delta^{13}C$ during the same time period. However, it is not known which phytoplankton community has the greatest affect on carbon isotope fractionation.

The trends seen between $\delta^{13}C$, dissolved oxygen, pH, and nutrient concentration show the effect of photosynthesis on carbon isotope fractionation in Crystal Lake. As the amount of biomass increases, $\delta^{13}C$ increases. This is because ^{12}C is preferentially taken up by algae during photosynthesis; the greater the biomass, the greater the rate of photosynthesis, leaving the residual water column more enriched in ^{13}C.

The amount of biomass also has a notable effect on nutrient concentrations. Trends exist between measured $\delta^{13}C$ values and the concentration of nutrients. Nutrients taken up by algae, such as phosphate and calcium, decrease over time in zones of high algal activity. This decrease in concentration corresponds to an increase in the measured $\delta^{13}C$ values. Trends can be seen between $\delta^{13}C$ values and parameters such as limnological strata, dissolved oxygen, and pH, as well as with the concentrations of silica, calcium, magnesium, and sodium. However, more research should be conducted to verify these results.

6.0 Future studies

There are several other studies that would help to corroborate the results of this study. For one, a sufficient amount of sample can be collected for algae identification, quantification, and the carbon isotope analysis of biomass. This should be done using a device similar to a van Dorn bottle to prevent cell damage during collection.

As for chlorophyll analysis, the use of HPLC (high performance liquid chromatography) could result in more specified analysis of chlorophyll and its degradation products. Different studies have found different wavelengths that may better estimate the amounts of chlorophyll than those used by the Standard Methods (Eaton, et al, 1995). For example, Faust (1982) found best wavelengths for measuring concentrations of each type of chlorophyll with variations in accessory pigments are: 553 nm for C_a, 642 nm for C_b, and 606 nm for C_c . The absorption bands for some accessory pigments could also be included in chlorophyll analysis to get a more precise identification of different algal types, and a better indication of the presence of cyanobacteria.

The above information could then be combined with counts of the different types of phytoplankton using microscope analysis. In this way, it may be possible to quantify the amounts of chlorophyll measured using either HPLC or spectrophotometer analysis, which could then be used to more accurately correlate algae communities with δ13C values.

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APPENDICES

A. Chemical Data

17 May 2007

Depth (ft)	Depth (m)	SiO_2 (mg/L)	Corrected SiO_2	PO_4^{-3} (mg/L)	NO_3^--N (mg/L)	Na^+ (ppm)	K^+ (ppm)	Mg^+ (ppm)	Ca^+ (ppm)	NH_4-N (ppm)	Cl^- (ppm)	SO_4 (ppm)	NO_3-N (ppm)
0.7	0.2	2.3	1.5	0.07	0.2	19.31	1.56	24.10	66.34		39.27	31.70	trace
5.2	1.6	2.5	1.7	0.12	0.1	20.71	1.71	24.71	67.68		40.43		
10.1	3.1	1.5	0.7	0.15	0.1	20.62	1.72	23.76	69.84		40.35	32.45	0.11
15.2	4.6	2.4	1.6	0.12	0.1	20.45	1.81	24.33	70.83		40.88	32.99	
20.2	6.1	2.1	1.3	0.13	0.1	22.01	1.96	25.35	72.94				
25.1	7.7	3.9	3.1	0.11	0.1	22.51	2.23	25.81	73.82	1.37	42.05	36.31	
30.0	9.1	5.2	4.4	0.17	0.1	22.77	2.47	26.60	75.93	2.19	42.92	34.65	trace
35.0	10.7	7.7	6.9	0.61	0.1	23.99	2.78	28.24	81.08	3.96	43.19	33.68	
36.2	11.0	10.6	9.8	1.02	0.1	25.23	2.87	29.15	83.89	4.24	44.50	34.96	

18 June 2007

Depth (ft)	Depth (m)	SiO_2 (mg/L)	Corrected SiO_2	PO_4^{-3} (mg/L)	NO_3^--N (mg/L)	Na^+ (ppm)	K^+ (ppm)	Mg^+ (ppm)	Ca^+ (ppm)	NH_4-N (ppm)	Cl^- (ppm)	SO_4 (ppm)	NO_3-N (ppm)
0.6	0.2	3.4	2.6	0.09	0.1	23.00	2.17	28.41	69.72		43.95	33.41	trace
4.9	1.5	2.4	1.6	0.10	0.1	22.27	2.10	27.64	68.16		44.00	34.01	0.05
10.3	3.1	1.9	1.1	0.10	0.1	24.25	2.06	25.55	73.08		42.75	34.88	0.64
15.1	4.6	3.1	2.3	0.14	0.1	23.00	2.26	24.67	73.27		43.18	34.96	
20.2	6.1	6.0	5.2	0.18	0.1	23.12	2.24	25.38	75.88		44.82	35.69	trace
24.6	7.5	4.1	3.3	0.09	0.0	22.08	3.02	25.82	77.15	1.81	45.72	35.93	trace

17 July 2007

Depth (ft)	Depth (m)	SiO_2 (mg/L)	Corrected SiO_2	PO_4^{-3} (mg/L)	NO_3^--N (mg/L)	Na^+ (ppm)	K^+ (ppm)	Mg^+ (ppm)	Ca^+ (ppm)	NH_4-N (ppm)	Cl^- (ppm)	SO_4 (ppm)	NO_3-N (ppm)
0.7	0.2	3.3	2.5	0.14	0.3	26.01	2.42	26.68	63.55		45.12	33.73	1.45
5.2	1.6	4.0	3.2	0.05	0.3	23.72	2.25	26.55	63.24		45.63	34.34	trace
10.0	3.1	3.9	3.1	0.06	0.1	23.15	2.22	26.70	63.90		46.90	34.05	trace
15.2	4.6	3.1	2.3	0.05	0.1	23.34	2.10	25.64	74.19		53.76	36.13	
20.1	6.1	4.9	4.1	0.14	0.1	22.20	2.36	26.09	77.86		51.50	37.23	
25.1	7.7	5.8	5.0	0.15	0.1	22.26	2.88	26.46	78.10	1.95	52.85	34.16	
30.2	9.2	8.1	7.3	0.84	0.1	23.90	3.23	26.99	79.85	3.00	53.61	34.70	
32.4	9.9	10.2	9.4	0.78	5.5	24.87	3.45	27.80	83.06	4.95	50.31	36.51	trace

2 August 2007

Depth (m)	SiO_2 (mg/L)	Corrected SiO_2	PO_4^{-3} (mg/L)	NO_3^--N (mg/L)	Na^+ (ppm)	K^+ (ppm)	Mg^+ (ppm)	Ca^+ (ppm)	NH4-N (ppm)	Cl^- (ppm)	SO_4 (ppm)	NO_3-N (ppm)
0.3	4.6	3.8	0.04	0.7	22.33	2.54	27.42	63.83		48.71	36.22	trace
5.1	4.7	3.9	0.04	0.8	22.78	2.23	26.64	69.15		47.53	36.24	trace
9.8	5.9	5.1	0.02	0.6	25.31	3.08	26.57	78.66	2.72	49.53	28.17	trace

17 August 2007

Depth (m)	SiO_2 (mg/L)	Corrected SiO_2	PO_4^{-3} (mg/L)	NO_3^--N (mg/L)	Na^+ (ppm)	K^+ (ppm)	Mg^+ (ppm)	Ca^+ (ppm)	NH_4-N (ppm)	Cl^- (ppm)	SO_4 (ppm)	NO_3-N (ppm)
0.4	4.3	3.5	0.06	0.7	16.52	1.09	16.99	18.66	2.95	48.41	36.23	trace
5.0	5.1	4.3	0.05	0.8	16.79	1.40	19.12	27.41		47.43	36.31	
9.7	9.5	8.7	0.54	0.9	16.64	1.26	19.15	48.96		48.22	27.53	trace
9.6	10.4	9.6	0.71	0.7	16.87	1.20	20.19	61.48	3.08	48.07	8.05	0.07

2 October 2007

Depth (ft)	Depth (m)	SiO_2 (mg/L)	Corrected SiO_2	PO_4^{-3} (mg/L)	NO_3^--N (mg/L)	Na^+ (ppm)	K^+ (ppm)	Mg^+ (ppm)	Ca^+ (ppm)	NH_4-N (ppm)	Cl^- (ppm)	SO_4 (ppm)	NO_3-N (ppm)
0.7	0.2	1.3	0.5	0.04	0.0	19.24	1.19	21.32	47.90		49.15	37.30	trace
5.1	1.6	2.8	2.0	0.04	0.0	18.59	1.19	21.84	47.97		48.03	36.20	0.12
9.9	3.0	1.0	0.2	0.02	0.1	19.09	1.17	22.42	49.01		51.33	41.32	
14.9	4.5	1.9	1.1	0.05	0.0	19.79	1.22	22.71	49.96		48.80	37.17	0.1
18.5	5.6	1.8	1.0	0.06	0.1	19.61	1.79	23.07	69.66	1.84			

5 October 2007

Depth (ft)	Depth (m)	SiO_2 (mg/L)	Corrected SiO_2	PO_4^{-3} (mg/L)	NO_3^--N (mg/L)	Na^+ (ppm)	K^+ (ppm)	Mg^+ (ppm)	Ca^+ (ppm)	NH_4-N (ppm)	Cl^- (ppm)	SO_4 (ppm)	NO_3-N (ppm)
0.7	0.2	4.80	4.00	0.175	0.10	19.82	1.67	23.30	67.90		49.65	37.02	trace
5.1	1.5	4.50	3.70	0.120	0.10	20.41	1.85	24.68	53.80		49.35	37.47	
10.0	3.0	6.20	5.40	0.102	0.20	20.54	1.92	24.68	53.80		49.79	37.20	
15.1	4.6	4.40	3.60	0.121	0.10	21.39	1.93	25.29	55.18		48.00	36.27	
20.1	6.1	3.00	2.20	0.053	0.10	21.37	2.04	25.39	61.86		49.08	38.68	trace
25.0	7.6	4.40	3.60	0.005	0.10						49.66	23.64	
30.1	9.2	8.40	7.60	0.657	0.10	21.60	2.13	25.06	74.92		49.89	20.10	0.07
33.6	10.2	10.0	9.20	1.42	0.60	24.31	3.00	26.20	79.04	3.88	49.73	32.35	trace

9 October 2007

Depth (ft)	Depth (m)	SiO_2 (mg/L)	Corrected SiO_2	PO_4^{-3} (mg/L)	NO_3^--N (mg/L)	Na^+ (ppm)	K^+ (ppm)	Mg^+ (ppm)	Ca^+ (ppm)	NH_4-N (ppm)	Cl^- (ppm)	SO_4 (ppm)	NO_3-N (ppm)
0.8	0.3	5.0	4.2	0.084	0.1	24.28	3.47	27.13	85.06	6.98	50.19	37.71	
5.0	1.5	4.1	3.3	0.115	0	23.82	2.29	26.94	58.22		50.17	37.21	0.4
10.0	3.1	4.4	3.6	0.037	0.1	24.49	2.38	27.02	59.26		51.71	41.16	
15.1	4.6	5.0	4.2	0.127	0.2	26.09	2.58	27.62	59.76		49.87	37.37	trace
20.0	6.1	14.10	13.3	0.041	0.20	24.03	2.09	26.79	66.91		51.52	39.89	trace
25.1	7.6	6.90	6.1	0.026	0.20	24.71	2.56	27.00	77.44		50.85	24.12	
30.1	9.2	11.70	10.9	0.620	0.10	23.75	3.56	27.35	81.74	3.35	50.98	9.15	0.08
35.0	10.7	17.70	16.9	2.108	0.10	23.29	2.85	25.01	75.31	4.89	50.54	10.09	0.24
37.8	11.5	18.70	17.9	2.842	0.10	28.27	5.00	29.75	98.01	9.01	48.55	8.49	0.22

B. Field Data

17 May 2007

Depth (ft)	Depth (m)	Temp (℃)	Sp. Cond. (µs/cm)	DO (mg/L)	pH	ORP	Corrected ORP	Alkalinity (meq/L)	Alkalinity (mg/L HCO_3^-)	Alkalinity (as $CaCO_3$)
0.7	0.2	20.02	608	9.2	8.22	294	498	0.77	46.74	261
2.4	0.7	19.96	603	9.2	8.24	301	505			
3.6	1.1	19.90	599	9.2	8.24	300	504			
5.2	1.6	19.81	593	9.3	8.23	302	506	0.78	47.72	256
6.6	2.0	19.46	582	9.5	8.21	306	510			
8.2	2.5	17.40	560	12.0	8.19	307	511			
10.1	3.1	*12.00*	*577*	*18.7*	*8.51*	*309*	513	0.82	50.07	244
11.7	3.6	10.54	593	20.6	8.57	314	518			
13.1	4.0	9.28	590	21.6	8.64	316	520			
15.2	4.6	8.28	611	24.0	8.75	317	521	0.83	50.90	240
16.7	5.1	7.66	585	25.1	8.77	323	527			
18.4	5.6	6.62	600	20.5	8.30	326	530			
20.2	6.1	5.79	607	9.7	7.83	328	532	0.82	49.80	245
22.2	6.8	5.09	617	1.6	7.47	332	536			
23.5	7.2	4.78	621	0.9	7.46	225	429			
25.1	7.7	4.50	623	0.4	7.44	53	257	0.72	43.94	278
26.9	8.2	4.36	623	0.3	7.41	4	208			
28.2	8.6	4.27	628	0.4	7.40	-8	196			
30.0	9.1	4.34	636	0.3	7.36	-70	134	0.71	43.52	280
32.3	9.8	4.45	648	0.2	7.31	-92	112			
33.8	10.3	4.54	657	0.4	7.28	-98	106			
35.0	10.7	4.72	671	0.3	7.23	-124	80	0.70	42.81	285
36.2	11.0	4.92	686	0.1	7.05	-146	58	0.64	39.31	310

18 June 2007

Depth (ft)	Depth (m)	Temp (°C)	Sp. Cond. (µs/cm)	DO (mg/L)	pH	ORP	Corrected ORP	Alkalinity (meq/L)	Alkalinity (mg/L HCO_3^-)	Alkalinity (as $CaCO_3$)
0.6	0.2	28.25	651	8.8	8.45	276	480	0.80	49.06	249
1.2	0.4	26.67	627	8.8	8.28	214	418			
3.1	0.9	26.39	623	8.2	8.26	208	412			
4.9	1.5	26.22	623	7.7	8.13	183	387	0.84	51.33	238
6.4	1.9	25.30	617	8.7	8.12	182	386			
7.8	2.4	23.54	597	12.0	8.21	179	383			
10.3	3.1	18.43	588	18.5	8.27	170	374	0.91	55.24	258
11.6	3.5	16.06	601	22.8	8.32	168	372			
13.7	4.2	12.22	591	22.8	8.14	164	368			
15.1	4.6	9.88	592	24.5	8.05	163	367	0.79	48.09	254
16.8	5.1	8.50	562	24.9	7.96	165	369			
18.3	5.6	7.74	580	1.1	7.38	-53	151			
20.2	6.1	7.31	578	0.2	7.56	-79	125	0.77	46.80	261
22.4	6.8	6.91	564	0.2	7.59	-86	118			
24.2	7.4	6.76	560	0.2	7.60	-88	116			
24.6	7.5	5.49	558	0.6	7.62	-112	92	0.78	47.59	256

17 July 2007

Depth (ft)	Depth (m)	Temp (°C)	Sp. Cond. (µs/cm)	DO (mg/L)	pH	ORP	Corrected ORP	Alkalinity (meq/L)	Alkalinity (mg/L HCO_3^-)	Alkalinity (as $CaCO_3$)
0.7	0.2	29.17	588	7.9	9.08	236	440	0.93	56.92	214
2.2	0.7	26.96	583	6.9	8.96	236	440			
4.0	1.2	26.96	585	6.2	8.89	239	443			
5.2	1.6	26.30	582	5.9	8.93	244	448	0.85	51.91	235
6.5	2.0	26.19	582	5.9	8.83	240	444			
8.7	2.7	25.51	586	6.0	8.82	241	445			
10.0	3.1	23.69	597	8.1	8.88	248	452	0.83	50.55	241
12.1	3.7	19.79	590	10.2	8.82	248	452			
13.9	4.2	16.18	589	11.2	8.70	248	452			
15.2	4.6	13.56	592	10.7	8.66	254	458	0.80	48.87	250
16.7	5.1	11.06	602	9.5	8.39	257	461			
18.1	5.5	9.37	611	7.1	8.07	258	462			
20.1	6.1	7.39	620	0.8	7.66	261	465	0.63	38.32	318
21.9	6.7	6.53	623	0.3	7.40	170	374			
23.4	7.1	5.88	626	0.2	7.74	-30	174			
25.1	7.7	5.40	635	0.1	7.75	-86	118	0.62	37.77	323
27.4	8.3	5.07	641	0.1	7.75	-95	109			
28.9	8.8	4.97	651	0.1	7.77	-111	93			
30.2	9.2	4.98	652	0.1	7.81	-132	72	0.82	49.93	244
32.1	9.8	5.00	672	0.1	7.79	-139	65			
32.4	9.9	5.02	674	0.0	7.95	-155	49	0.84	51.12	239

2 August 2007

Depth (m)	Temp (℃)	Sp. Cond. (µs/cm)	DO (mg/L)	pH	ORP	Corrected ORP	Alkalinity (meq/L)	Alkalinity (mg/L HCO_3^-)	Alkalinity (as $CaCO_3$)
0.3	29.25	633	ND	8.15	245	449	0.96	58.56	208
1.8	27.3	631	ND	7.97	243	447			
3.3	25.73	629	ND	7.88	242	446			
5.1	19.99	632	ND	7.79	240	444	0.90	54.87	222
6.1	14.55	631	ND	7.39	233	437			
7.6	7.94	673	ND	6.74	233	437			
9.8	5.23	437	ND	6.70	64	268	0.86	52.59	232

ND = No Data

17 August 2007

Depth (m)	Temp (℃)	Sp. Cond. (µs/cm)	DO (mg/L)	pH	ORP	Corrected ORP	Alkalinity (meq/L)	Alkalinity (mg/L HCO_3^-)	Alkalinity (as $CaCO_3$)
0.4	28.03	612	0.0	8.18	170	374	0.93	56.74	215
1.7	27.66	613	0.0	8.08	169	373			
3.5	26.14	612	0.0	8.09	168	372			
5.0	22.83	604	0.0	8.06	182	386	0.92	56.05	218
6.3	15.91	527	0.0	7.88	184	388			
8.0	7.61	451	0.0	6.94	14	218			
9.7	5.34	728	0.0	6.84	-85	119	0.83	50.62	241
9.6	5.34	754	0.0	6.66	-95	109	0.84	51.26	238

2 October 2007

Depth (ft)	Depth (m)	Temp (℃)	Sp. Cond. (µs/cm)	DO (mg/L)	pH	ORP	Corrected ORP	Alkalinity (meq/L)	Alkalinity (mg/L HCO_3^-)	Alkalinity (as $CaCO_3$)
0.7	0.2	21.18	502	ND	7.96	-26	178	1.00	60.70	203
1.5	0.4	21.11	503	ND	7.94	-25	179			
3.9	1.2	20.94	503	ND	7.95	-27	178			
5.1	1.6	20.78	503	ND	7.95	-27	177	1.04	63.65	194
6.4	2.0	20.74	503	ND	7.99	-35	169			
8.2	2.5	20.67	504	ND	7.99	-35	169			
9.9	3.0	20.63	503	ND	7.98	-36	168	0.98	59.80	204
11.8	3.6	20.59	504	ND	8.02	-40	164			
13.5	4.1	20.14	510	ND	7.99	-40	164			
14.9	4.5	18.62	527	ND	7.86	-40	165	1.00	60.80	197
17.5	5.3	14.65	557	ND	7.44	-38	166			
18.6	5.7	13.52	565	ND	7.79	-174	30			
18.5	5.6	13.44	579	ND	7.72	-98	106	0.82	49.86	241

ND = No Data

5 October 2007

Depth (ft)	Depth (m)	Temp (°C)	Sp. Cond. (µs/cm)	DO (mg/L)	pH	ORP	Corrected ORP	Alkalinity (meq/L)	Alkalinity (mg/L HCO_3^-)	Alkalinity (as $CaCO_3$)
0.7	0.2	22.58	504	9.6	8.51	-39	165	1.03	62.56	195
1.5	0.5	22.07	503	9.9	8.53	-39	165			
3.5	1.1	21.63	505	9.5	8.45	-40	164			
5.1	1.5	21.14	502	10.1	8.53	-43	161	1.02	62.24	196
7.1	2.2	20.96	502	10.0	8.33	-44	160			
9.1	2.8	20.82	503	9.9	8.52	-44	160			
10.0	3.0	20.76	503	9.8	8.52	-45	159	0.98	59.51	205
11.9	3.6	20.58	504	9.8	8.49	-46	158			
13.1	4.0	19.65	512	11.6	8.43	-45	159			
15.1	4.6	18.06	531	13.7	8.31	-42	162	0.92	55.88	218
16.6	5.1	15.79	551	11.8	7.94	-37	167			
18.6	5.7	12.82	564	4.5	7.50	-40	164			
20.1	6.1	11.55	566	0.5	7.40	-46	158	0.83	50.76	240
22.1	6.7	8.99	574	0.2	7.39	-89	115			
23.6	7.2	7.74	580	0.1	7.33	-100	104			
25.0	7.6	6.86	589	0.1	7.37	-98	106	0.75	45.86	266
26.6	8.1	6.28	597	0.0	7.33	-85	119			
28.5	8.7	5.84	612	0.0	7.28	-87	117			
30.1	9.2	5.70	628	0.0	7.22	-87	117	0.67	40.89	298
31.5	9.6	5.07	646	0.0	7.13	-89	115			
33.6	10.2	5.65	677	0.0	6.97	-88	116	0.82	49.86	244

9 October 2007

Depth (ft)	Depth (m)	Temp (°C)	Sp. Cond. (µs/cm)	DO (mg/L)	pH	ORP	Corrected ORP	Alkalinity (meq/L)	Alkalinity (mg/L HCO_3^-)	Alkalinity (as $CaCO_3$)
0.8	0.3	23.27	506	8.9	8.35	-5	199	0.92	55.88	218
1.8	0.5	23.26	506	9.2	8.37	-8	196			
3.9	1.2	23.19	506	10.0	8.38	-8	196			
5.0	1.5	22.59	502	11.5	8.50	-6	198	1.03	62.89	194
6.8	2.1	21.87	502	11.6	8.51	-8	196			
8.1	2.5	21.59	502	11.5	8.49	-8	197			
10.0	3.1	21.19	502	11.3	8.47	-6	198	1.04	63.32	193
12.5	3.8	20.44	505	11.4	8.43	-7	197			
13.9	4.2	19.40	515	13.5	8.37	-6	198			
15.1	4.6	17.95	532	15.5	8.21	-5	199	0.93	56.92	214
16.8	5.1	15.14	554	10.7	7.71	-1	203			
18.8	5.7	12.93	562	4.1	7.35	-1	203			
20.0	6.1	11.62	564	1.1	7.26	-4	200	0.85	51.99	235
22.4	6.8	9.00	572	0.2	7.23	-48	156			
23.8	7.3	7.75	583	0.1	7.23	-77	127			
25.1	7.6	6.94	590	0.1	7.25	-79	125	0.79	48.48	252
26.9	8.2	6.30	595	0.0	7.27	-76	128			
28.6	8.7	5.90	606	0.0	7.24	-78	126			
30.1	9.2	5.73	624	0.0	7.20	-81	123	0.77	46.68	261
32.0	9.8	5.62	652	0.0	7.13	-78	126			
33.8	10.3	5.61	685	0.0	7.05	-74	130			
35.0	10.7	5.62	703	0.0	7.01	-70	134	0.57	34.59	353
36.8	11.2	5.68	732	0.0	6.95	-69	135			
37.8	11.5	5.71	740	0.0	6.91	-70	134	0.57	35.02	348

C. Chlorophyll Data

17 May 2007

Depth (ft)	Depth (m)	Ca (mg/m3)	Cb (mg/m3)	Cc (mg/m3)	Biomass (mg/m3)
0.7	0.2	0.0103	0.014	0.0151	0.689
5.2	1.6	0.0154	0.0163	0.0169	1.031
10.1	3.1	0.0147	0.0152	0.0201	0.987
15.2	4.6	0.0154	0.016	0.0196	1.031
20.2	6.1	0.1718	0.0066	0.0211	11.508
25.1	7.7	0.0402	0.0344	0.0225	2.694
30.0	9.1	0.0143	0.0171	0.0204	0.959
35.0	10.7	0.0346	0.0236	0.0252	2.316
36.2	11.0	0.0595	0.0142	0.0118	3.988

18 June 2007

Depth (ft)	Depth (m)	Ca (mg/m3)	Cb (mg/m3)	Cc (mg/m3)	Biomass (mg/m3)
0.6	0.2	0.0482	0.0194	0.0190	3.231
4.9	1.5	0.0175	0.0196	0.0253	1.173
10.3	3.1	0.0154	0.0093	0.0450	1.032
15.1	4.6	0.0626	0.0261	0.0401	4.194
20.2	6.1	0.0624	0.0176	0.0204	4.183
24.6	7.5	0.1174	0.0181	0.0161	7.869

17 July 2008

Depth (ft)	Depth (m)	Ca (mg/m3)	Cb (mg/m3)	Cc (mg/m3)	Biomass (mg/m3)
0.7	0.2	0.0145	0.0161	0.0195	0.972
5.2	1.6	0.0181	0.0183	0.0176	1.210
10.0	3.1	0.0187	0.0199	0.0187	1.250
15.2	4.6	0.0555	0.0091	0.0238	3.718
20.1	6.1	0.0534	0.0156	0.0204	3.576
25.1	7.7	0.0235	0.0136	0.0157	1.574
30.2	9.2	0.0171	0.0105	0.0248	1.146
32.4	9.9	0.0357	0.0171	0.0178	2.392

2 August 2007

Depth (m)	Ca (mg/m3)	Cb (mg/m3)	Cc (mg/m3)	Biomass (mg/m3)
0.3	0.0130	0.0132	0.0189	0.871
5.1	0.0166	0.0227	0.0305	1.111
9.8	0.0149	0.0121	0.0135	0.996

17 August 2007

Depth (m)	Ca (mg/m3)	Cb (mg/m3)	Cc (mg/m3)	Biomass (mg/m3)
0.4	0.0122	0.0117	0.0180	0.816
5.0	0.0286	0.0172	0.0181	1.915
9.7	0.0243	0.0139	0.0172	1.627
9.6	0.0237	0.0154	0.0197	1.585

2 October

Depth (ft)	Depth (m)	Ca (mg/m3)	Cb (mg/m3)	Cc (mg/m3)	Biomass (mg/m3)
0.7	0.2	0.0181	0.0227	0.0283	1.212
5.1	1.6	0.0152	0.0159	0.0280	1.016
9.9	3.0	0.0106	0.0085	0.0112	0.711
14.9	4.5	0.0210	0.0035	0.0192	1.404
18.5	5.6	0.0358	0.0083	0.0120	2.401

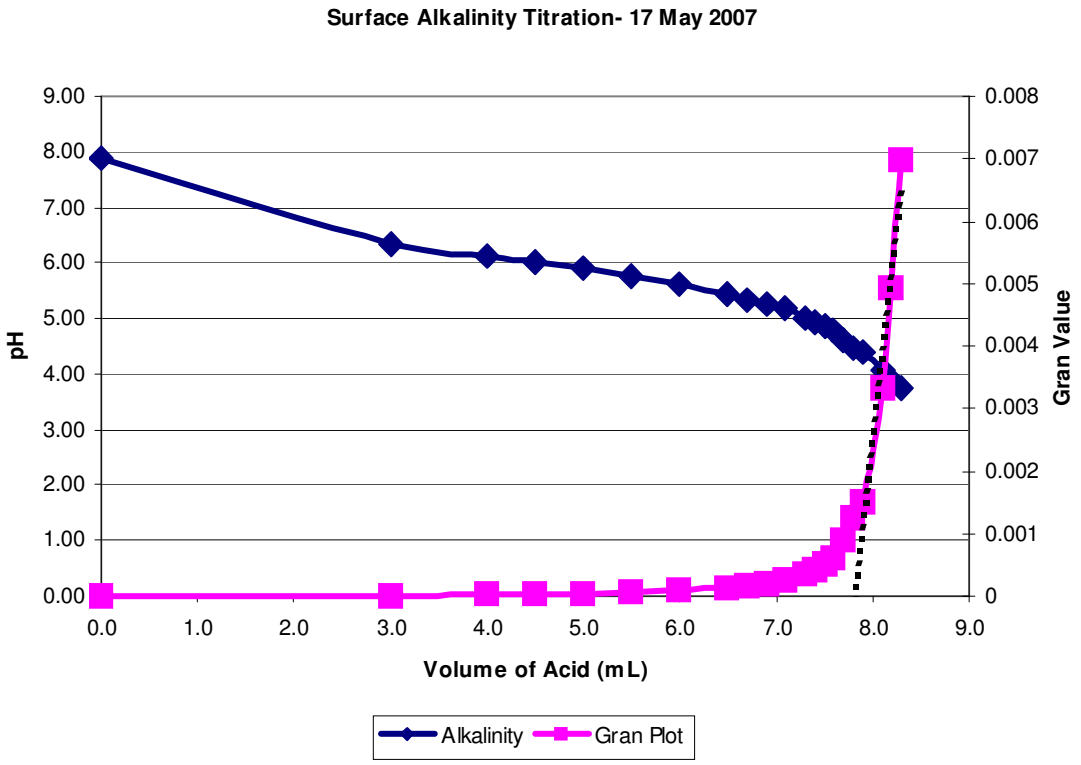
5 October 2007

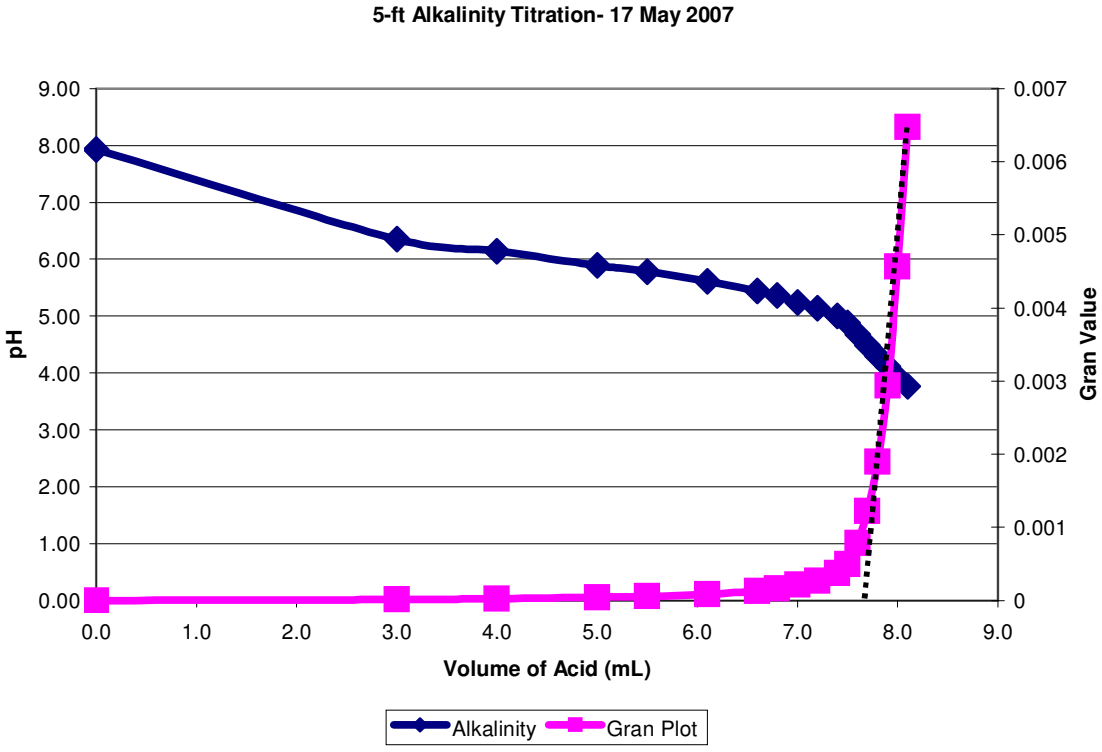
Depth (ft)	Depth (m)	Ca (mg/m3)	Cb (mg/m3)	Cc (mg/m3)	Biomass (mg/m3)
0.7	0.2	0.0181	0.0195	0.0252	1.2110
5.1	1.5	0.0139	0.0089	0.0085	0.933
10.0	3.0	0.0213	0.0179	0.0232	1.430
15.1	4.6	0.0224	0.0107	0.0085	1.498
20.1	6.1	0.0507	0.0164	0.0229	3.399
25.0	7.6	0.0115	0.0065	0.0017	0.772
30.1	9.2	0.0273	0.0181	0.0207	1.831
33.6	10.2	0.0180	0.0147	0.0151	1.203

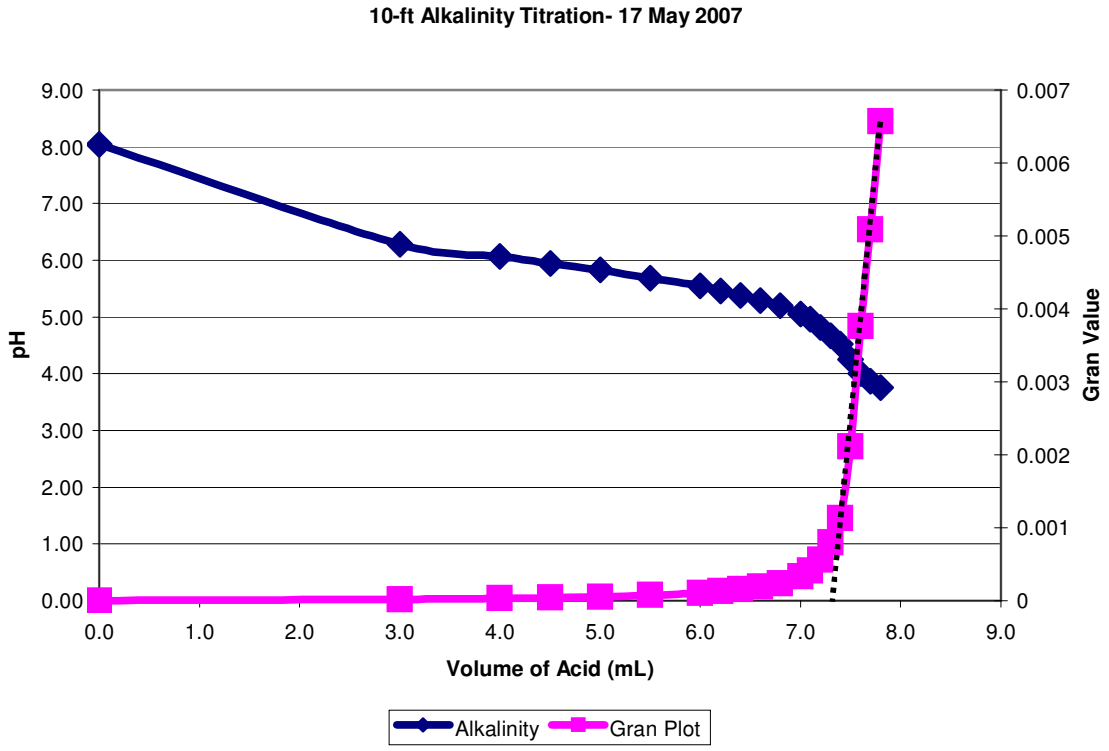
9 October 2007

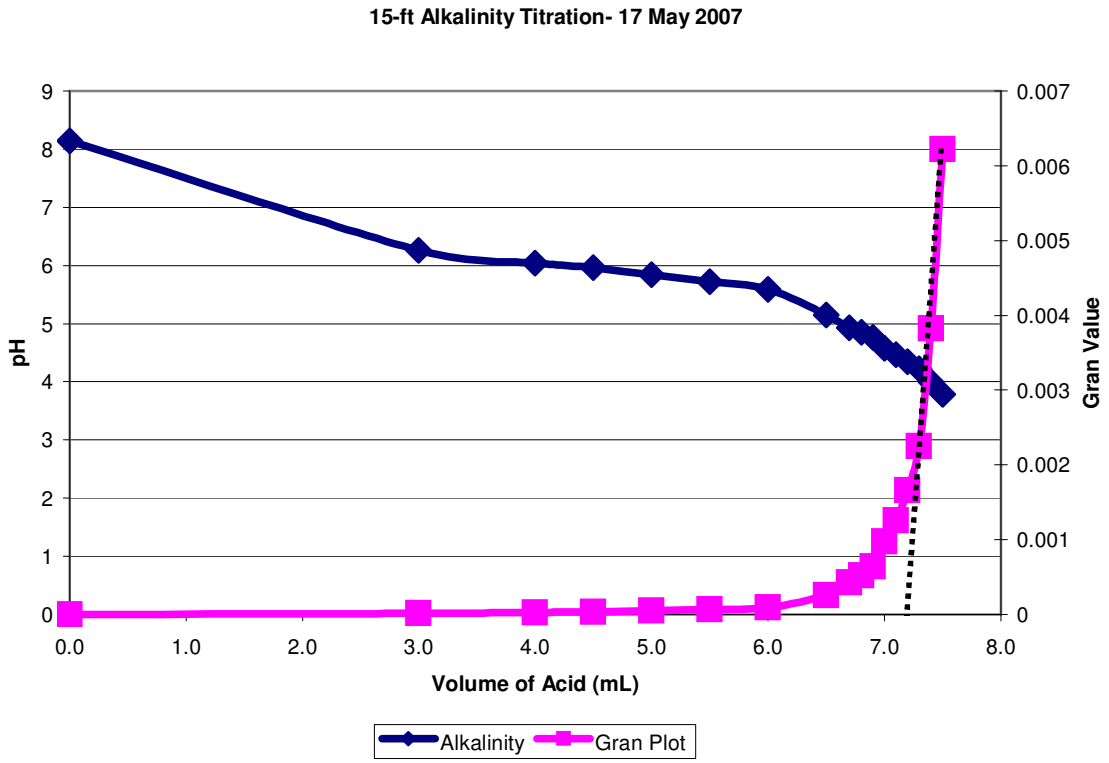
Depth (ft)	Depth (m)	Ca (mg/m3)	Cb (mg/m3)	Cc (mg/m3)	Biomass (mg/m3)
0.8	0.3	0.0155	0.0146	0.0184	1.040
5.0	1.5	0.0207	0.0180	0.0246	1.386
10.0	3.1	0.0224	0.0203	0.0258	1.501
15.1	4.6	0.0226	0.0115	0.0160	1.512
20.0	6.1	0.0602	0.0132	0.0229	4.031
25.1	7.6	0.0088	0.0059	0.0036	0.592
30.1	9.2	0.0178	0.0169	0.0180	1.193
35.0	10.7	0.0178	0.0153	0.0121	1.196
37.8	11.5	0.0036	-0.0069	0.0058	0.244

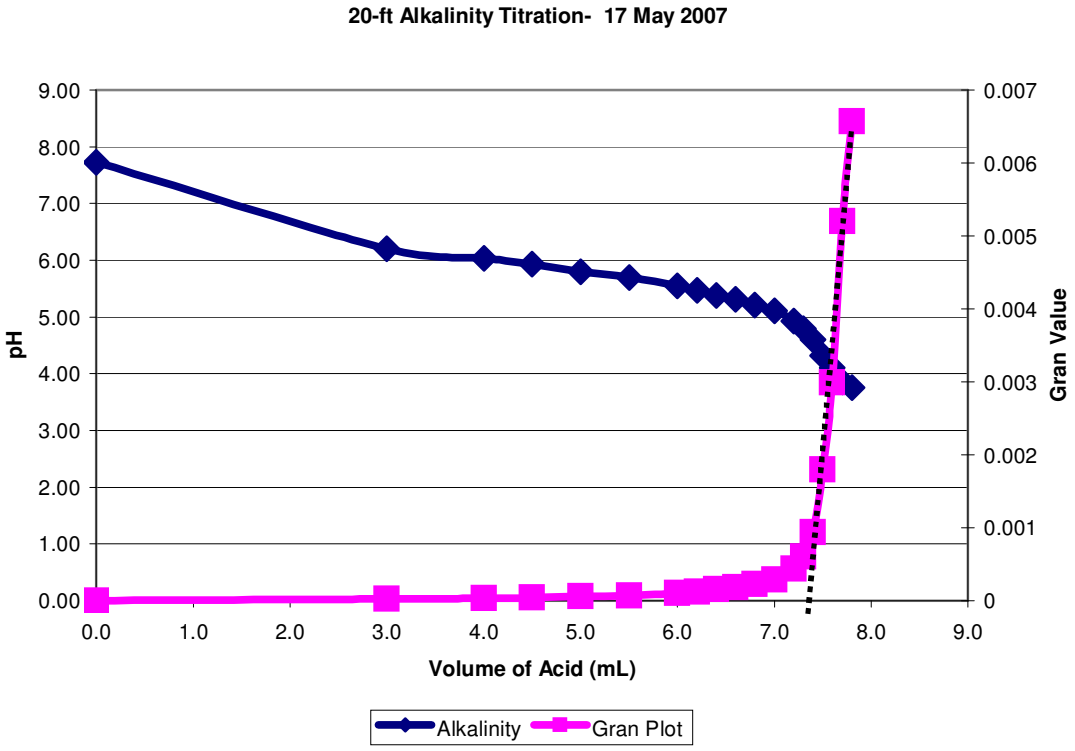
D. Alkalinity Titrations

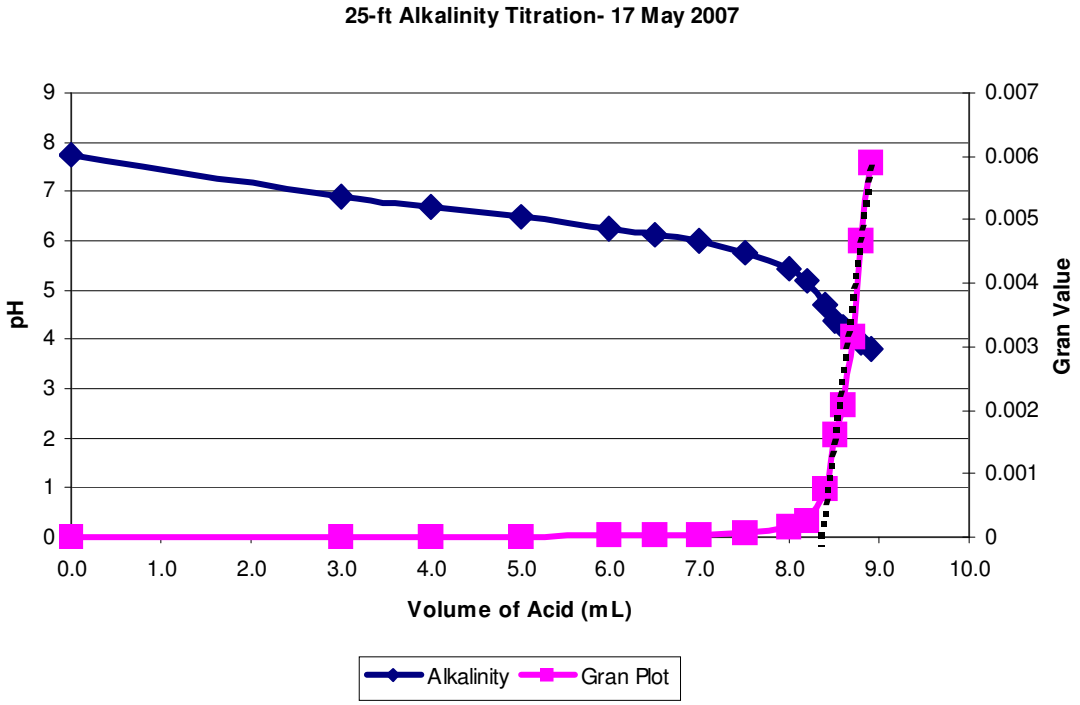


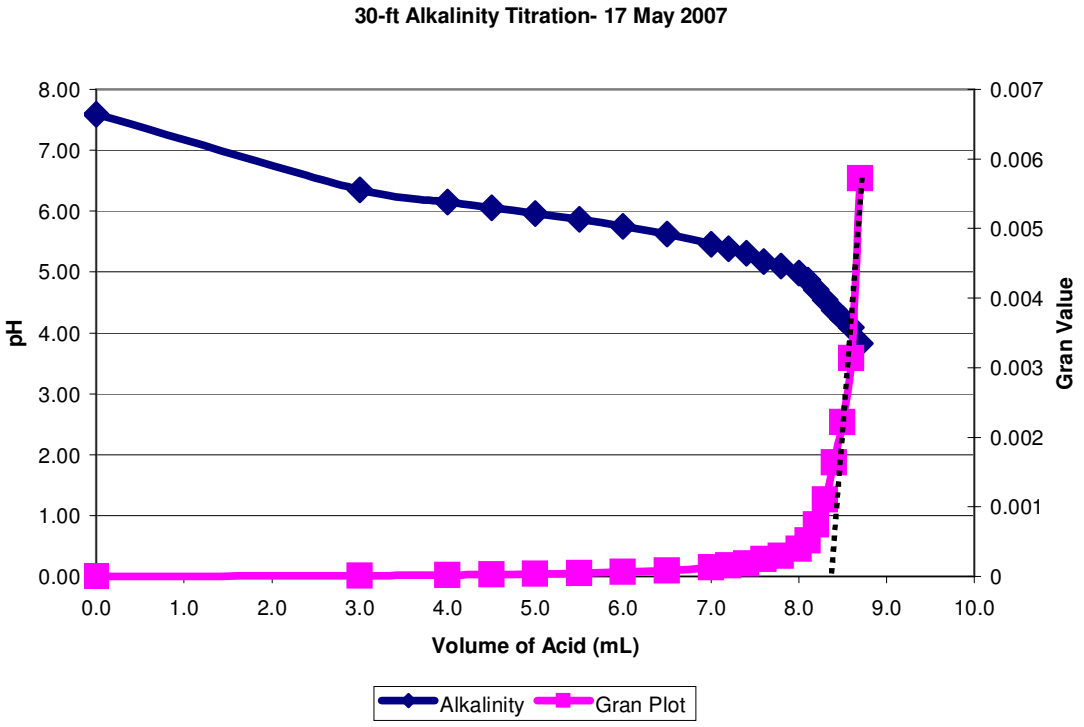


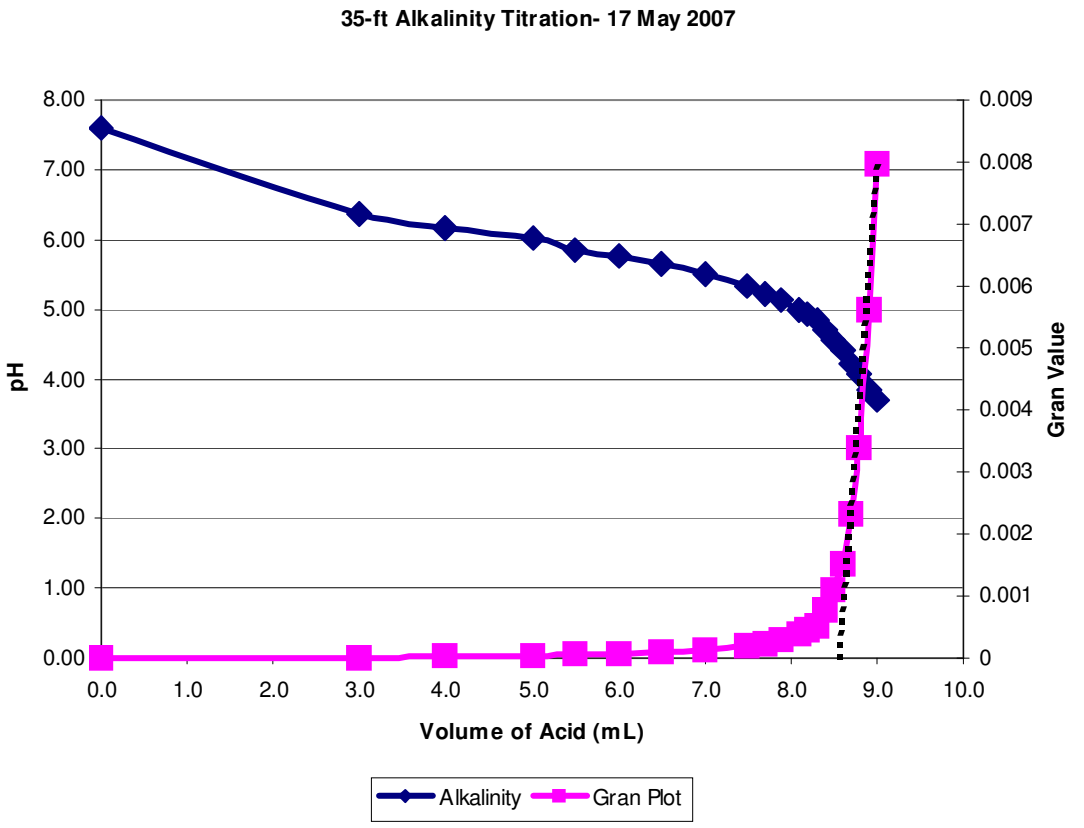

10-ft Alkalinity Titration- 17 May 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Volume of Acid (mL)
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
Alkalinity
Gran Plot

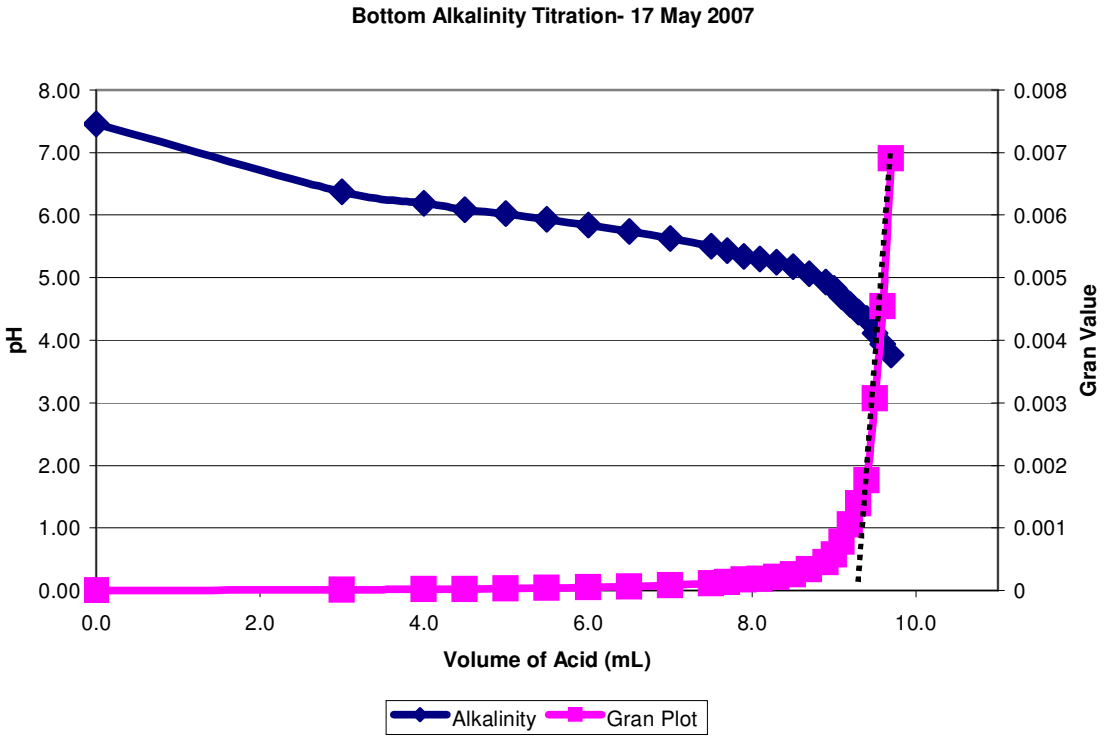

15-ft Alkalinity Titration- 17 May 2007
9
8
7
6
5
4
3
2
1
0
pH
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
Alkalinity
Gran Plot

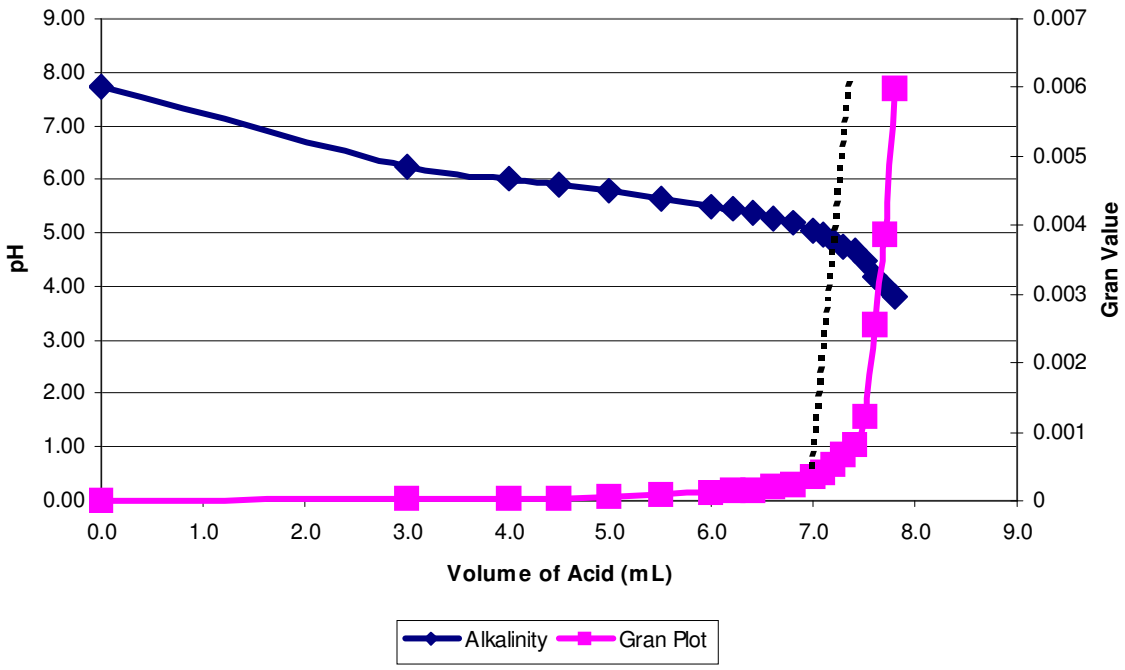

20-ft Alkalinity Titration- 17 May 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Volume of Acid (mL)
Alkalinity
Gran Plot

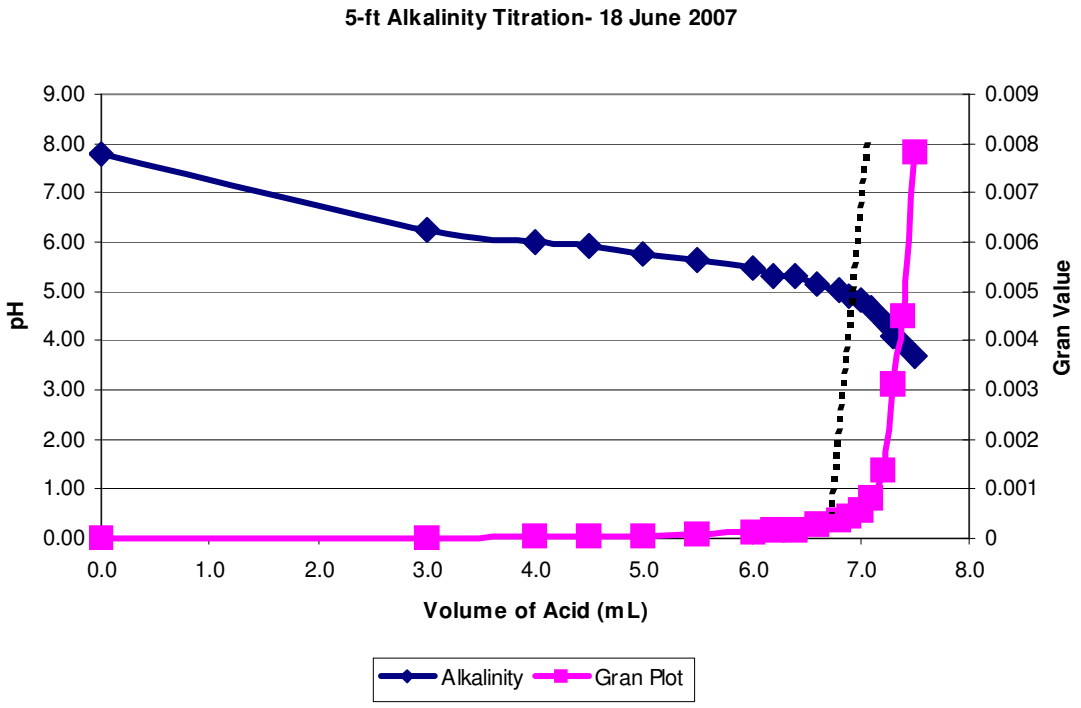

25-ft Alkalinity Titration- 17 May 2007
9
8
7
6
5
4
3
2
1
0
pH
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
Volume of Acid (mL)
Alkalinity
Gran Plot

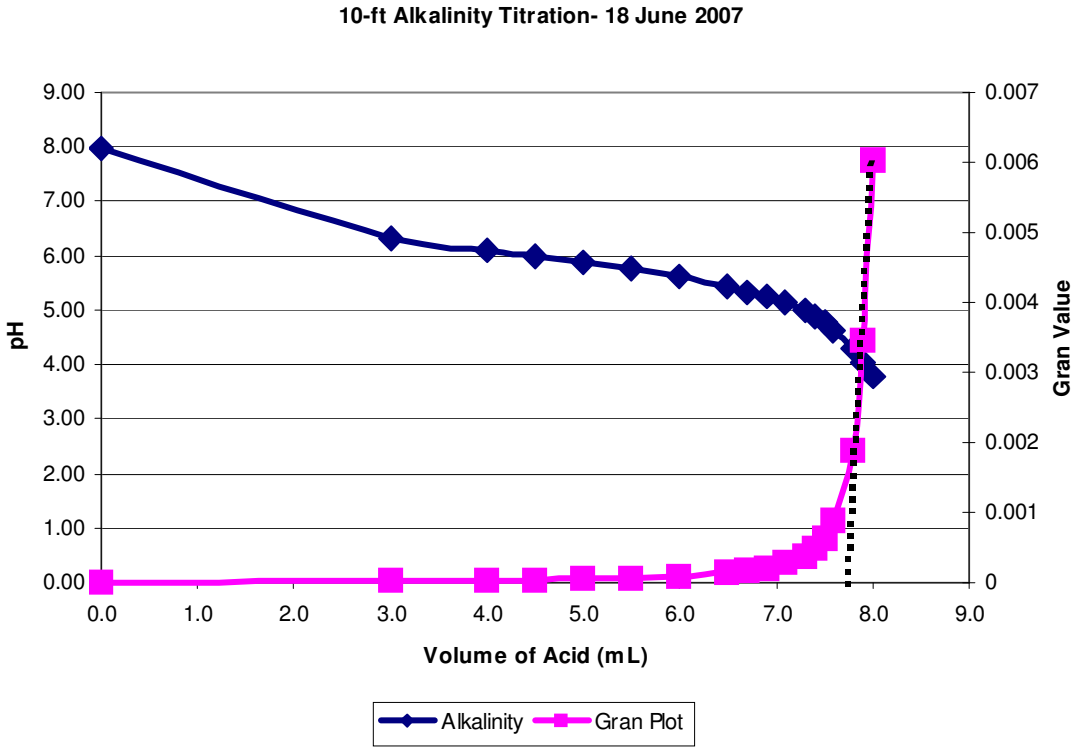

30-ft Alkalinity Titration- 17 May 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
Volume of Acid (mL)
Alkalinity
Gran Plot

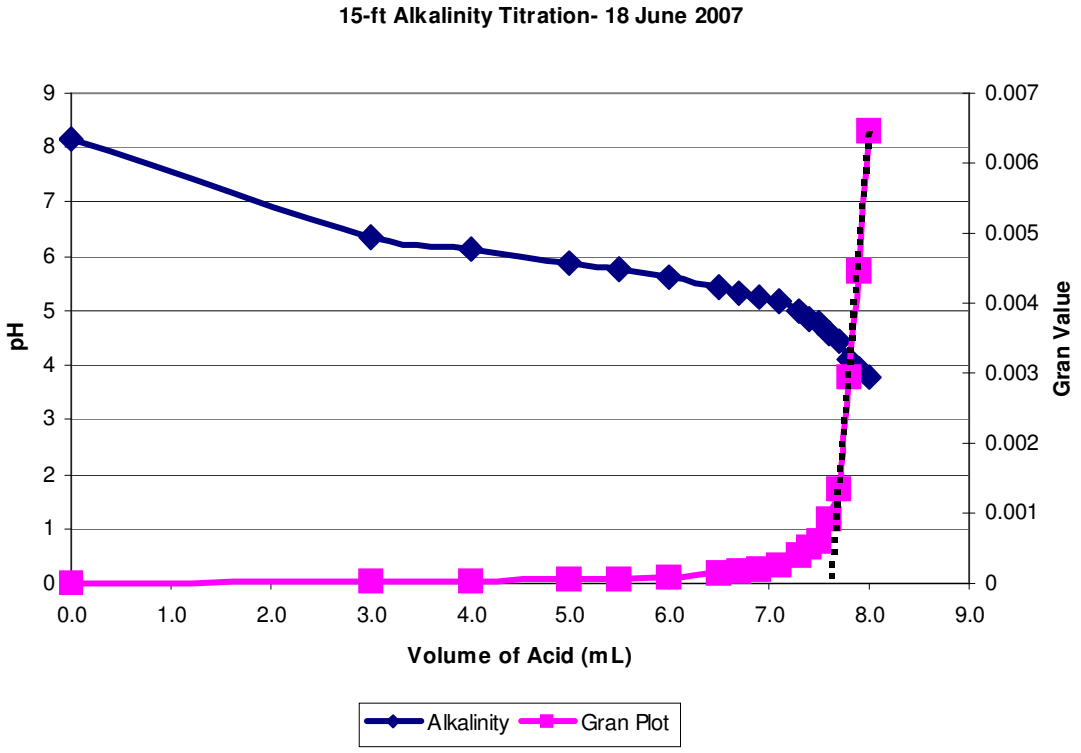

35-ft Alkalinity Titration- 17 May 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
Volume of Acid (mL)
Alkalinity
Gran Plot

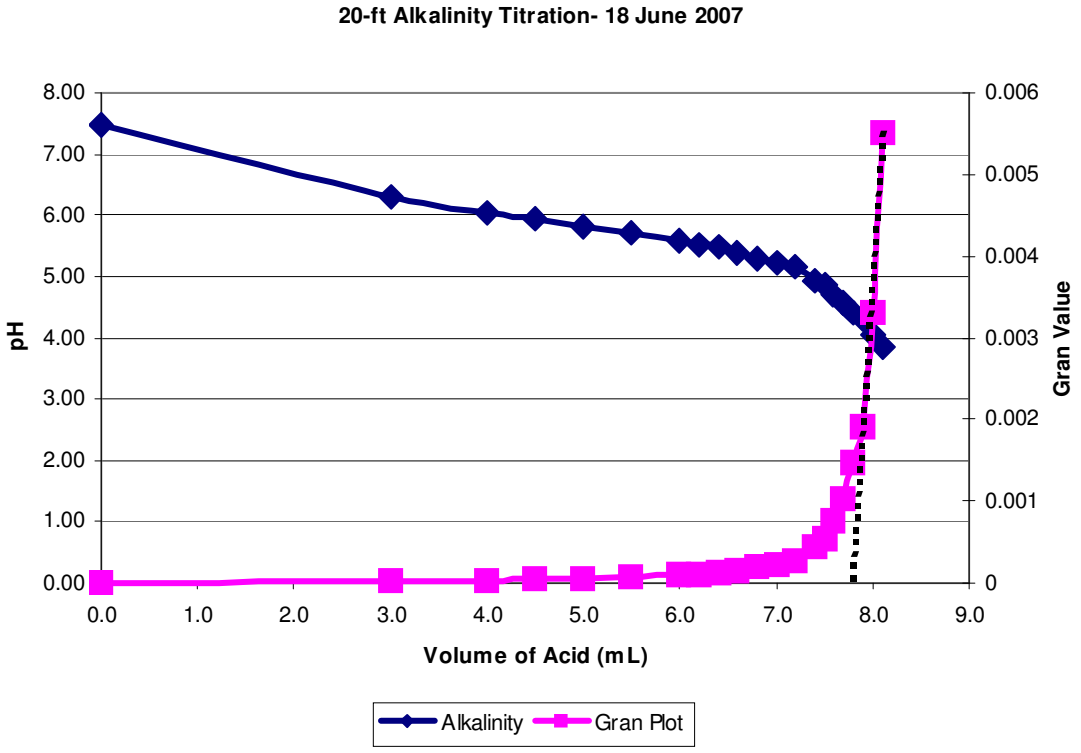

Bottom Alkalinity Titration- 17 May 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
2.0
4.0
6.0
8.0
10.0
Volume of Acid (mL)
Alkalinity
Gran Plot

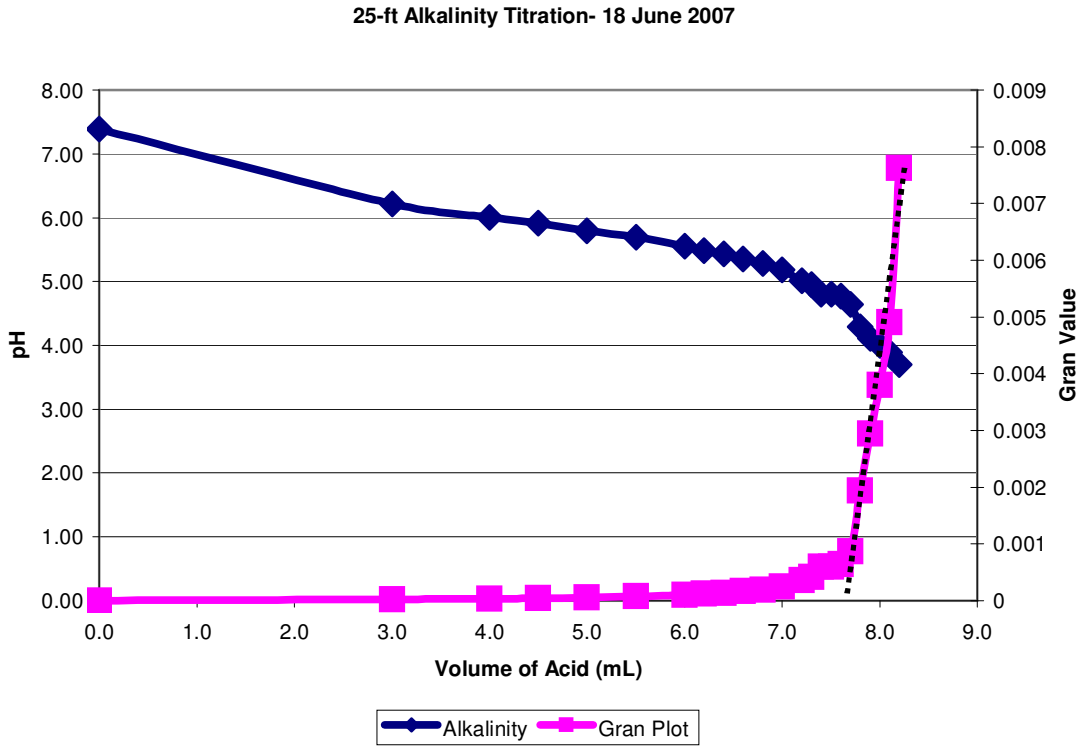

Surface Alkalinity Titration- 18 June 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Volume of Acid (mL)
Alkalinity
Gran Plot

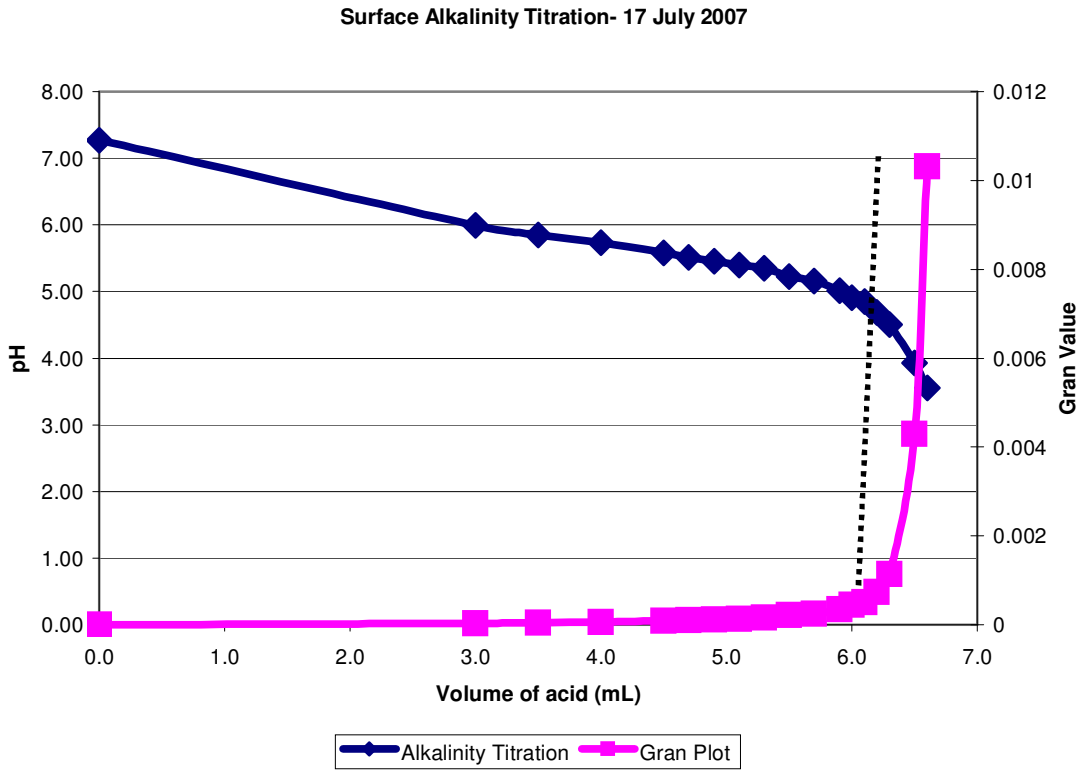

5-ft Alkalinity Titration- 18 June 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)
Alkalinity
Gran Plot

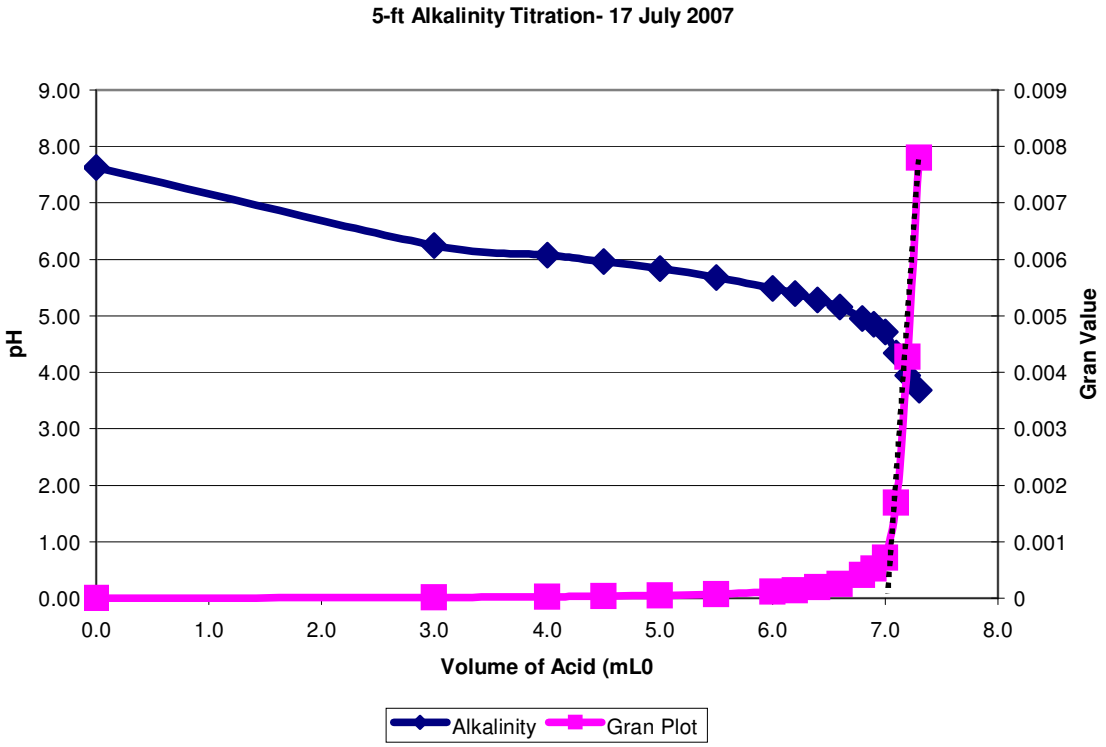

10-ft Alkalinity Titration- 18 June 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Volume of Acid (mL)
Alkalinity
Gran Plot

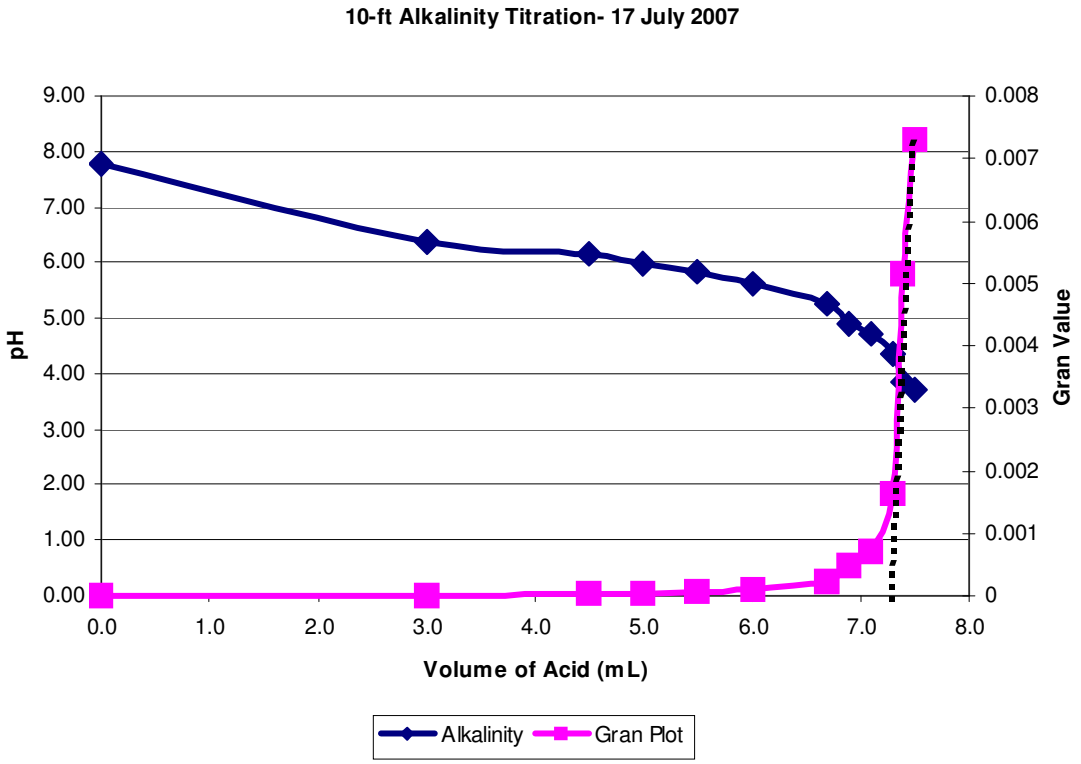

15-ft Alkalinity Titration- 18 June 2007
pH
Gran Value
Volume of Acid (mL)
Alkalinity
Gran Plot

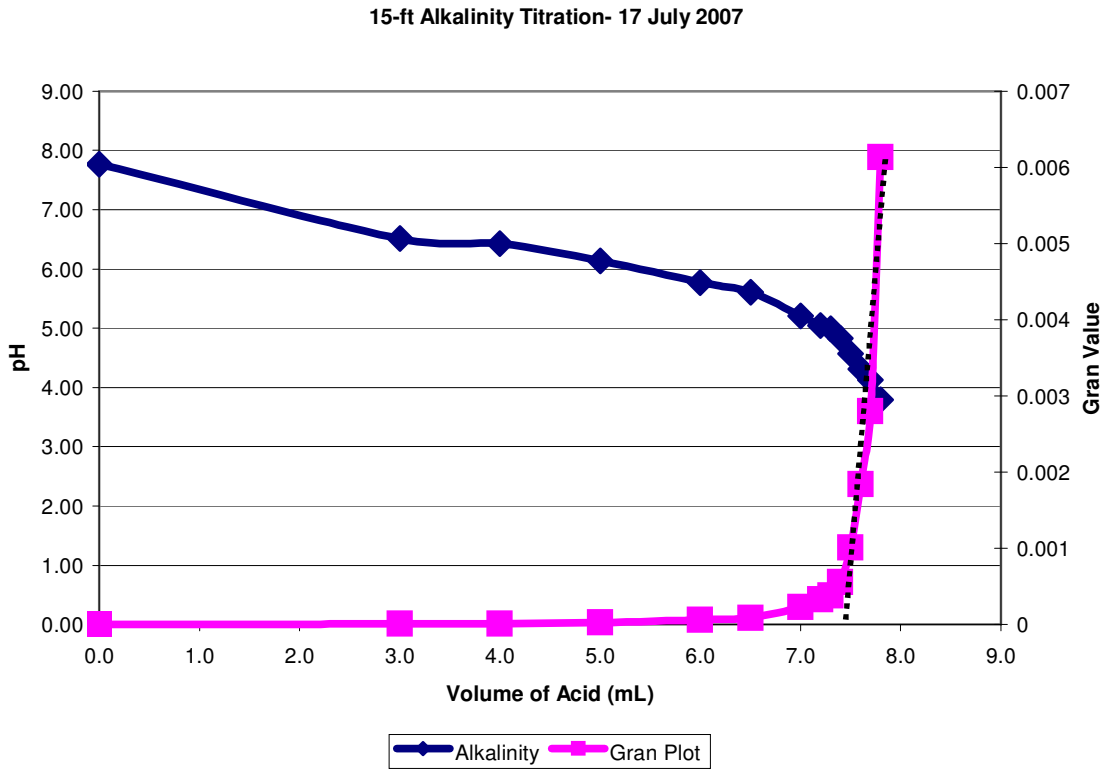

20-ft Alkalinity Titration- 18 June 2007
pH
Gran Value
Volume of Acid (mL)
Alkalinity
Gran Plot

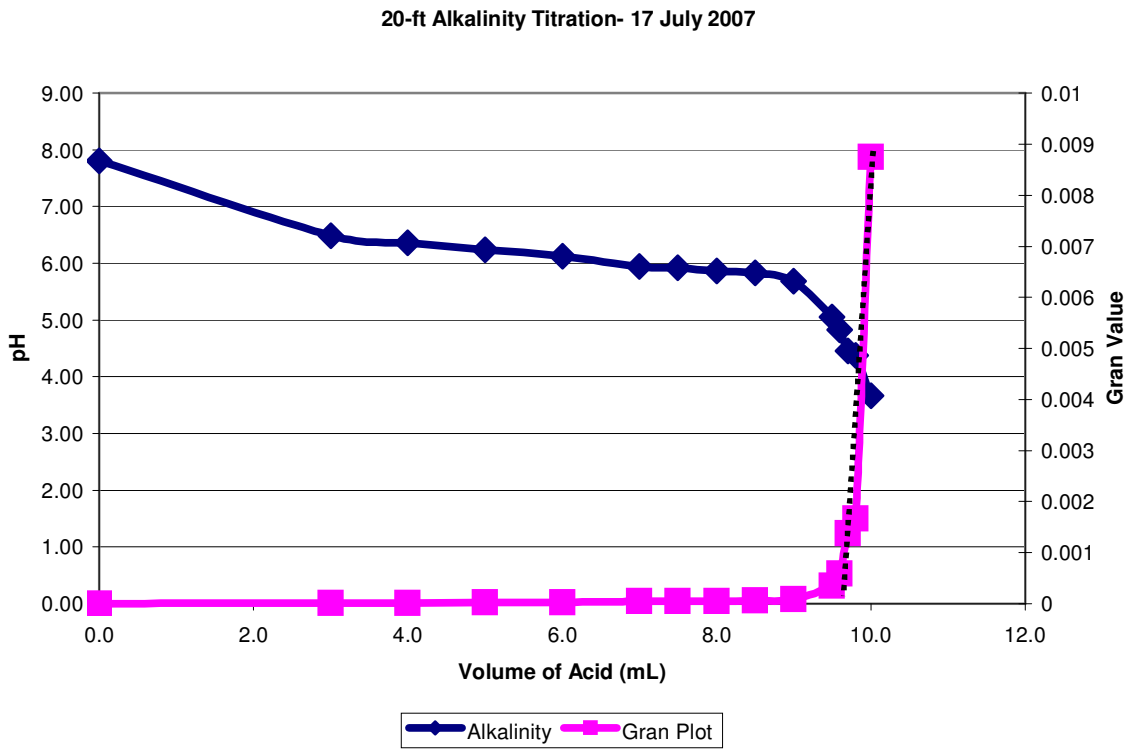

25-ft Alkalinity Titration- 18 June 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Volume of Acid (mL)
Alkalinity
Gran Plot

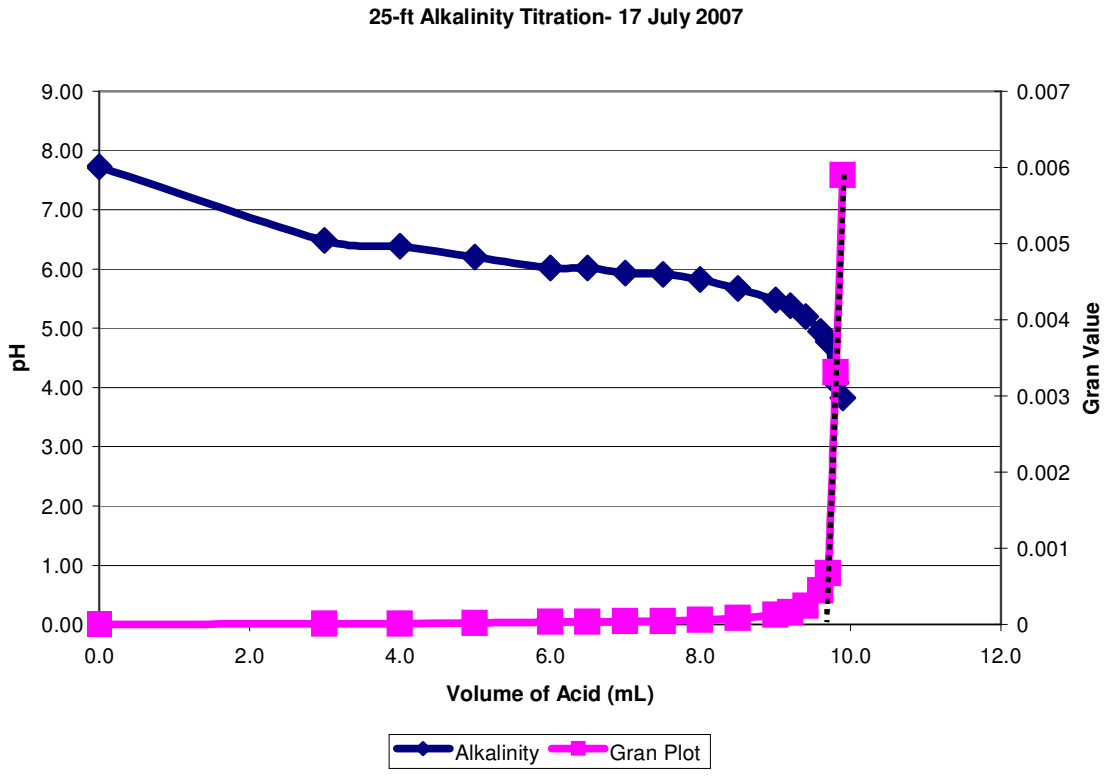

Surface Alkalinity Titration- 17 July 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.012
0.01
0.008
0.006
0.004
0.002
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Volume of acid (mL)
Alkalinity Titration
Gran Plot

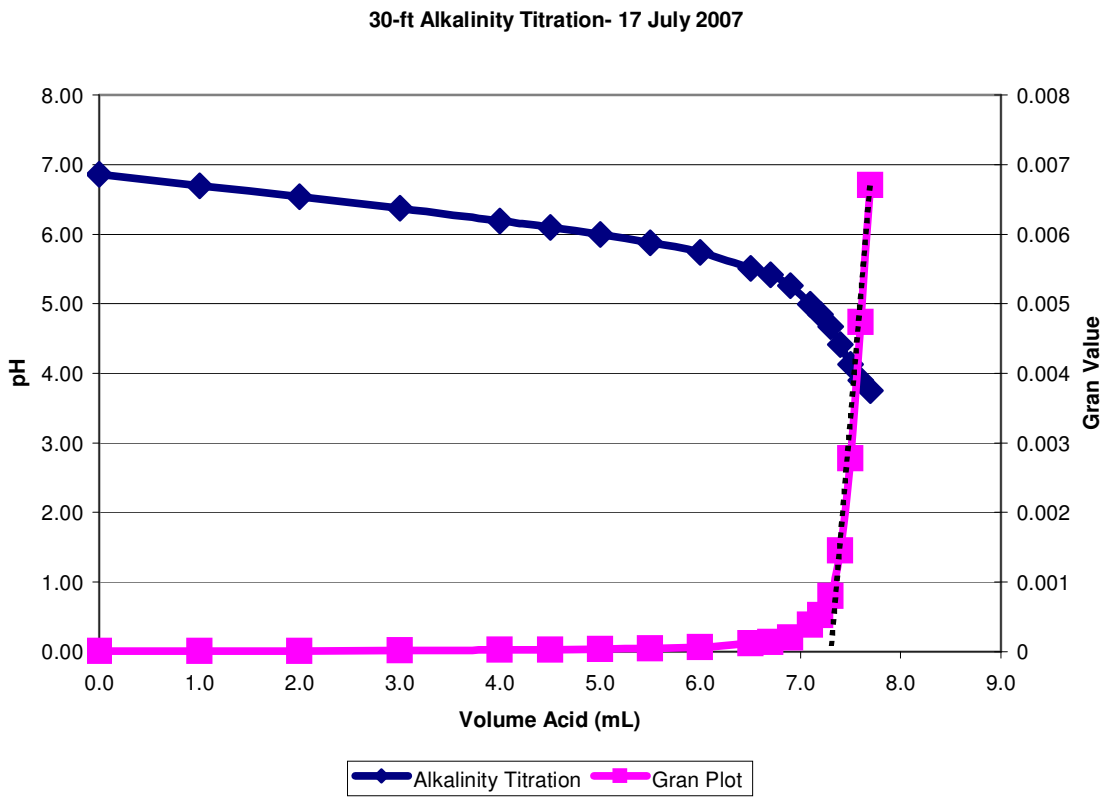

5-ft Alkalinity Titration- 17 July 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL0
Alkalinity
Gran Plot

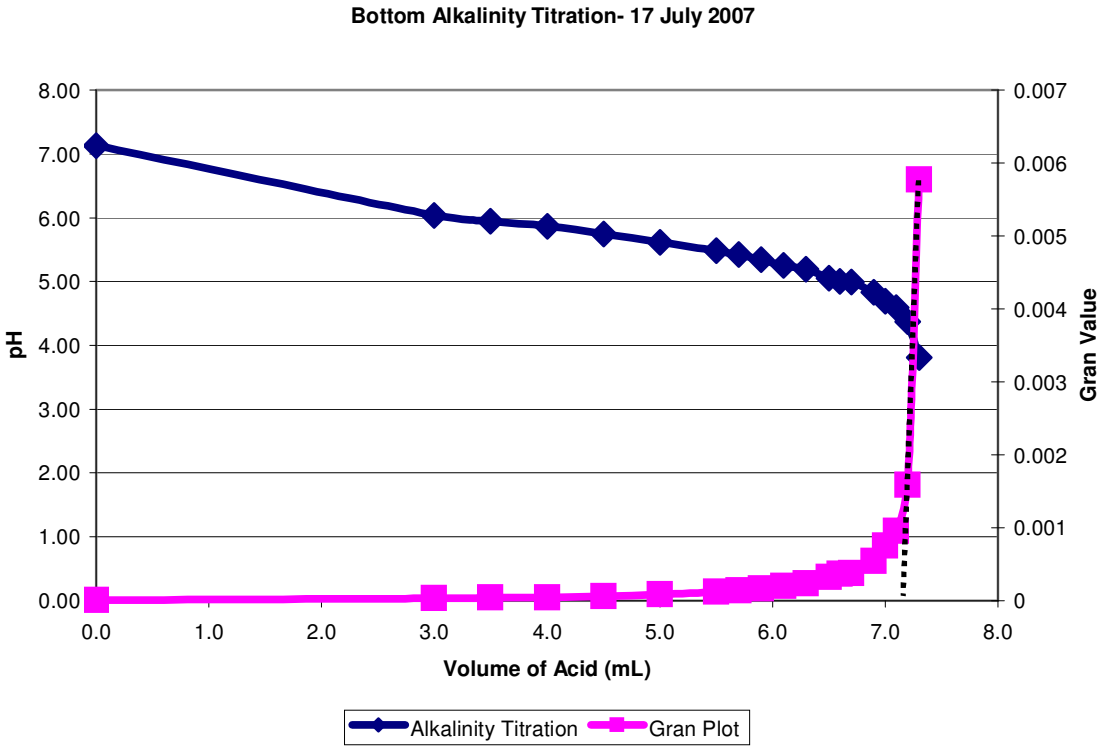

10-ft Alkalinity Titration- 17 July 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)
Alkalinity
Gran Plot

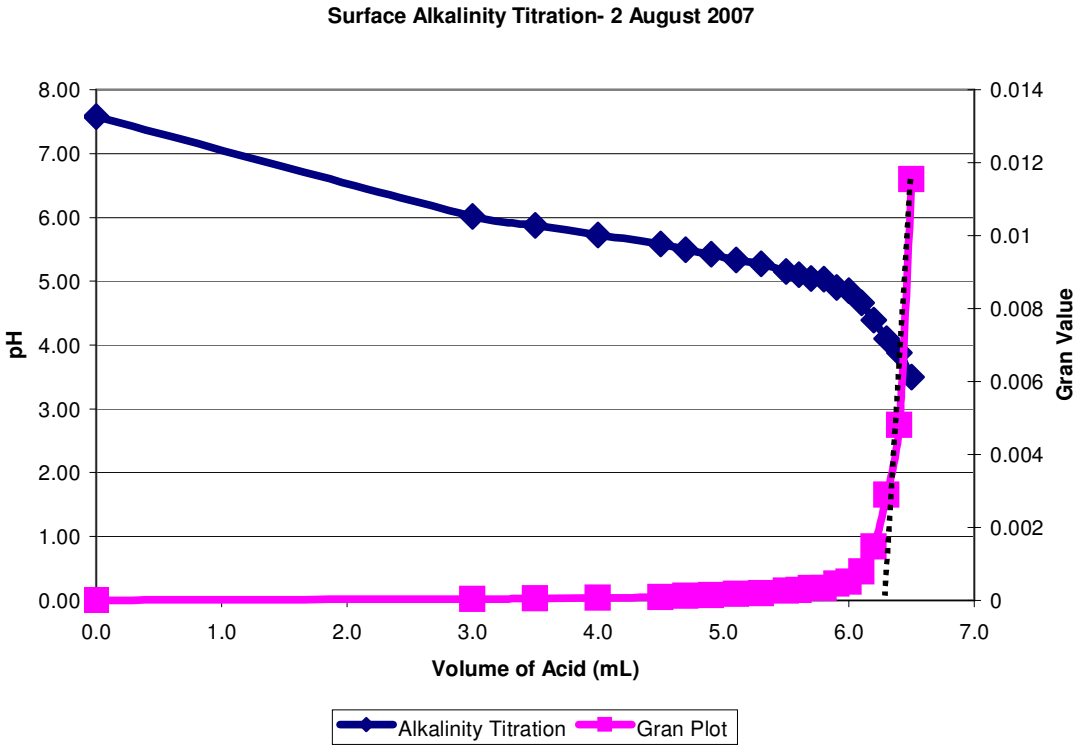

15-ft Alkalinity Titration- 17 July 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Volume of Acid (mL)
Alkalinity
Gran Plot

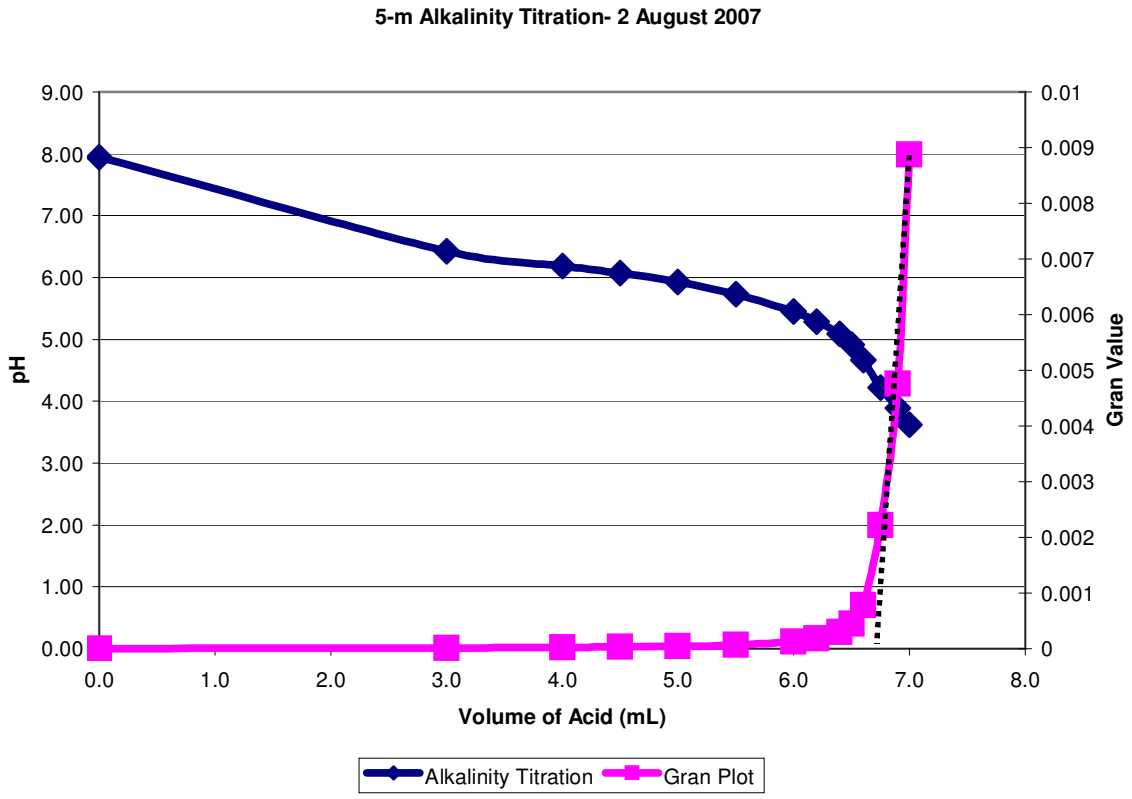

20-ft Alkalinity Titration- 17 July 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Volume of Acid (mL)
Alkalinity
Gran Plot

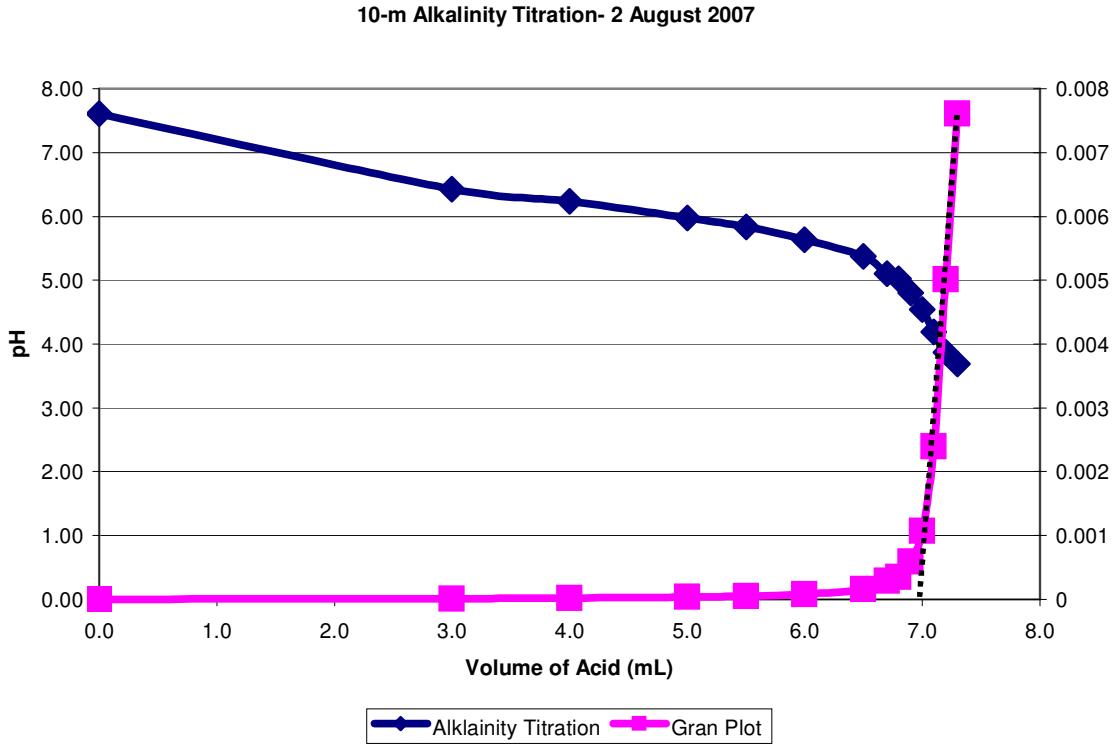

25-ft Alkalinity Titration- 17 July 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Volume of Acid (mL)
Alkalinity
Gran Plot

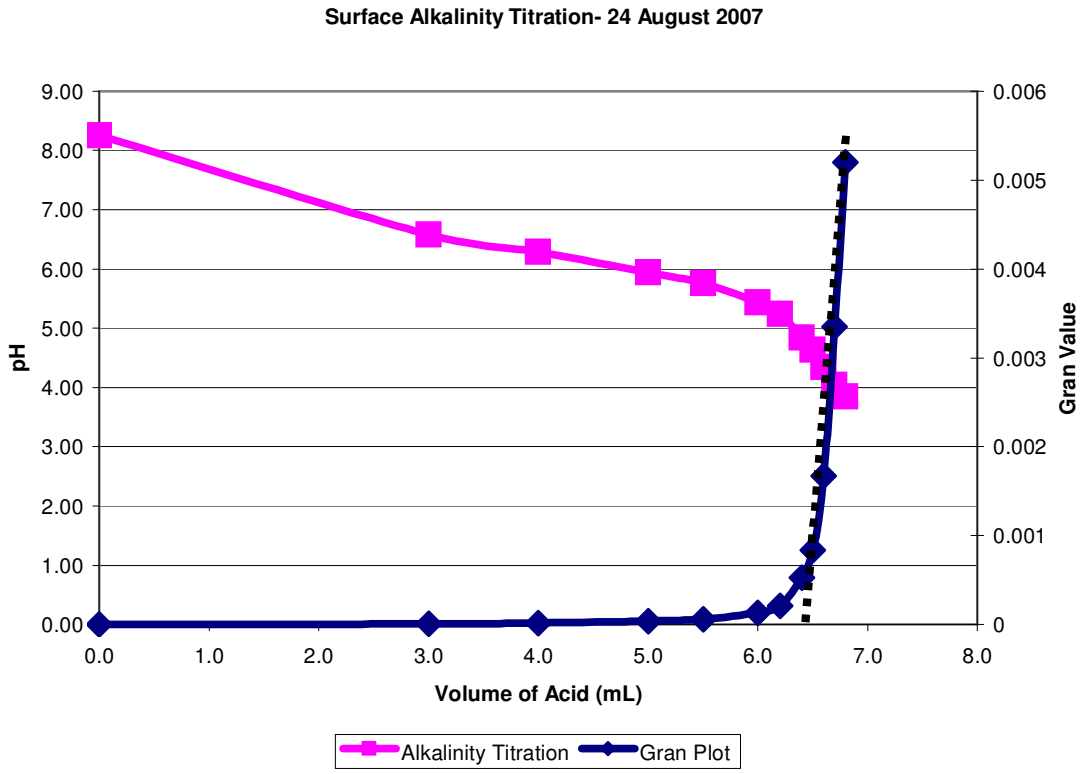

30-ft Alkalinity Titration- 17 July 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Volume Acid (mL)
Alkalinity Titration
Gran Plot

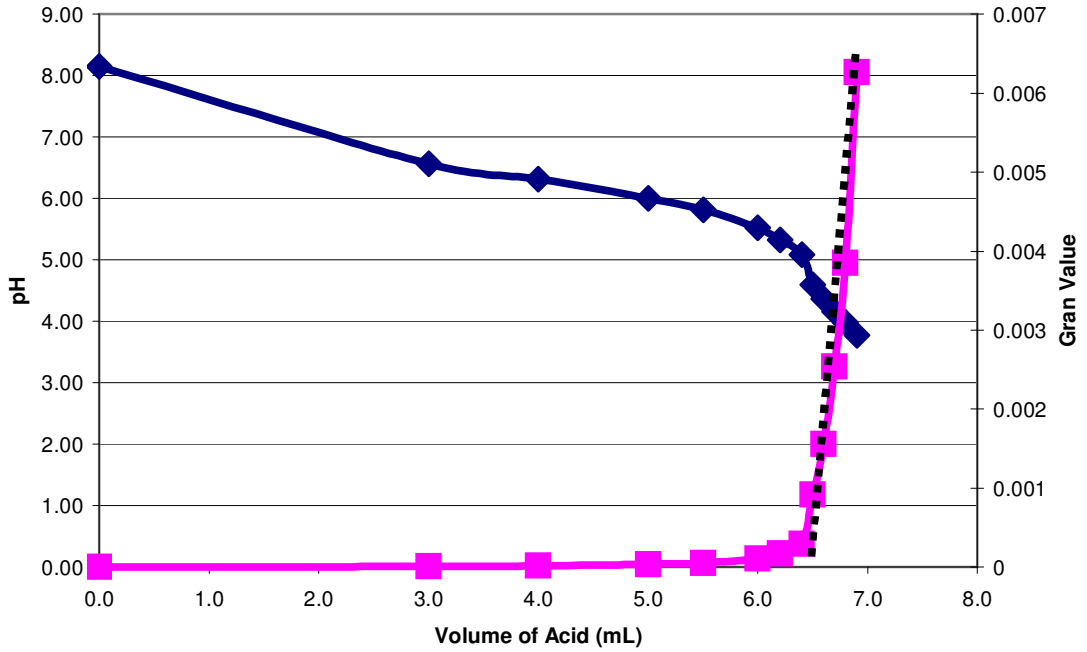

Bottom Alkalinity Titration- 17 July 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

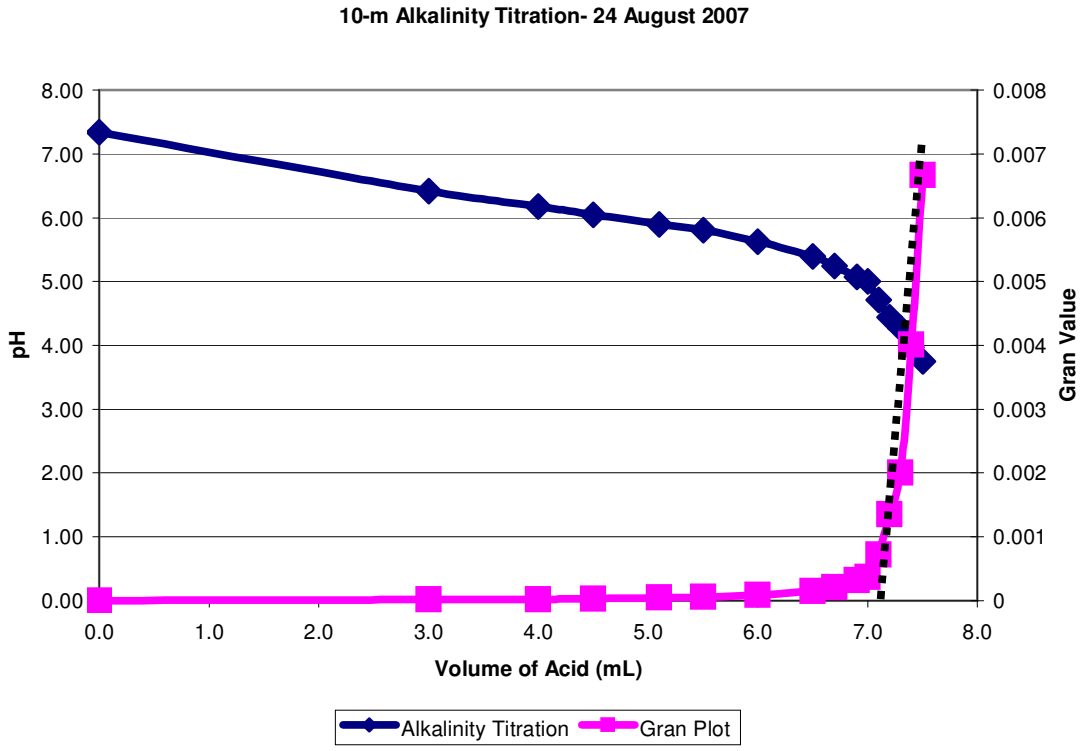

Surface Alkalinity Titration- 2 August 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

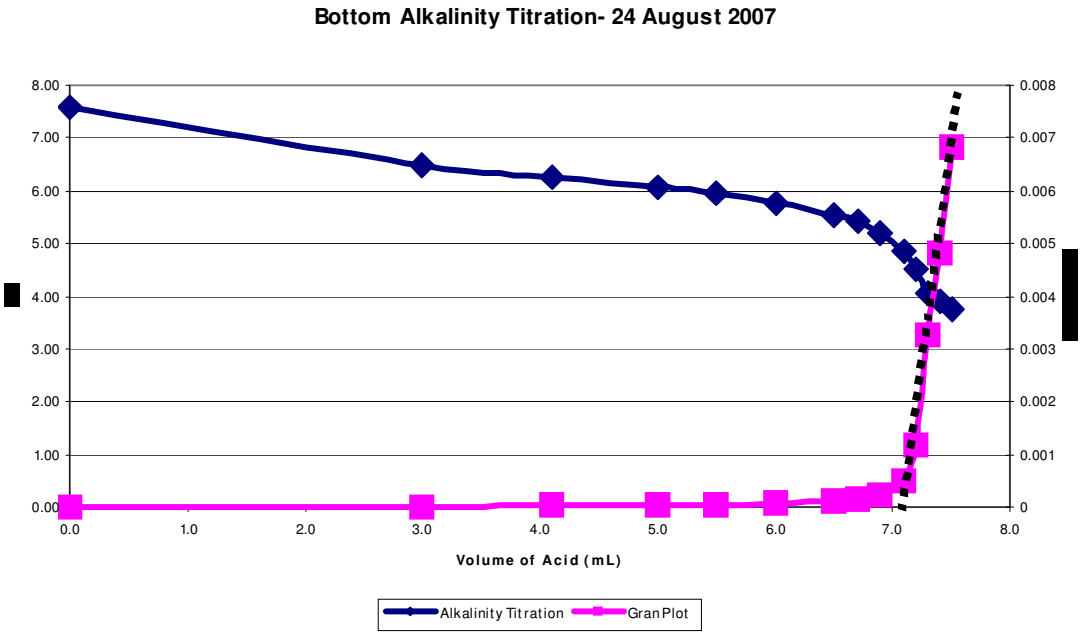

5-m Alkalinity Titration- 2 August 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

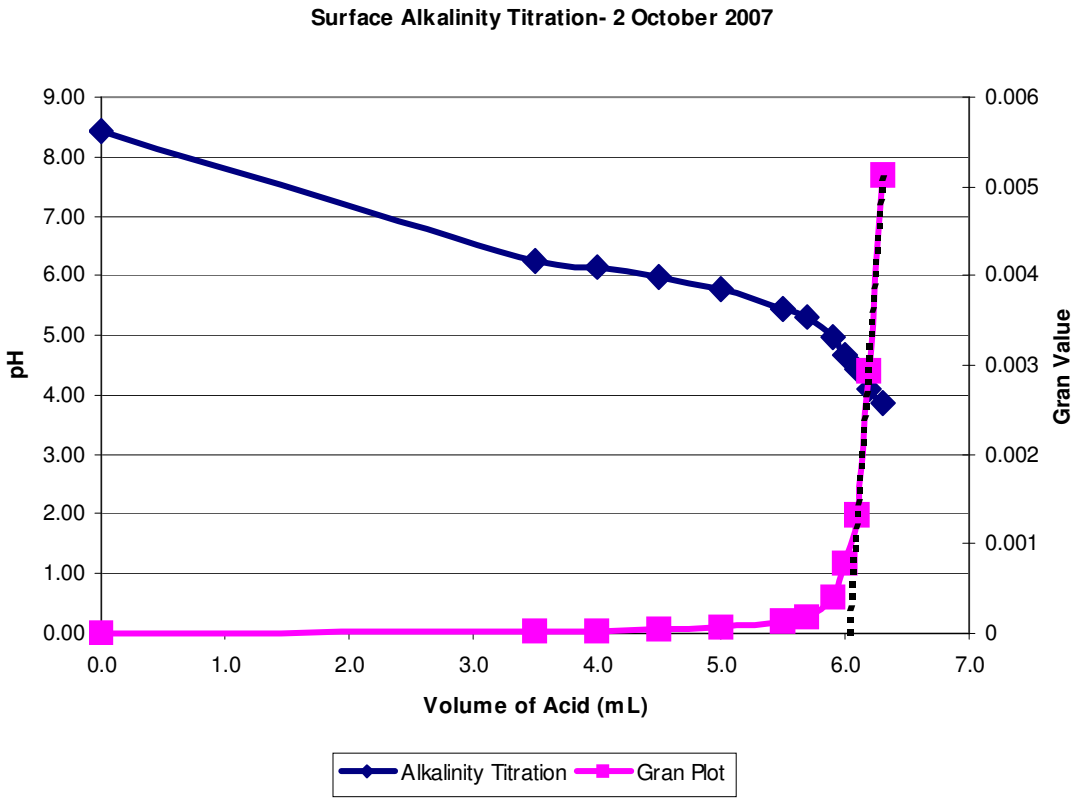

10-m Alkalinity Titration- 2 August 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)
Alklainity Titration
Gran Plot

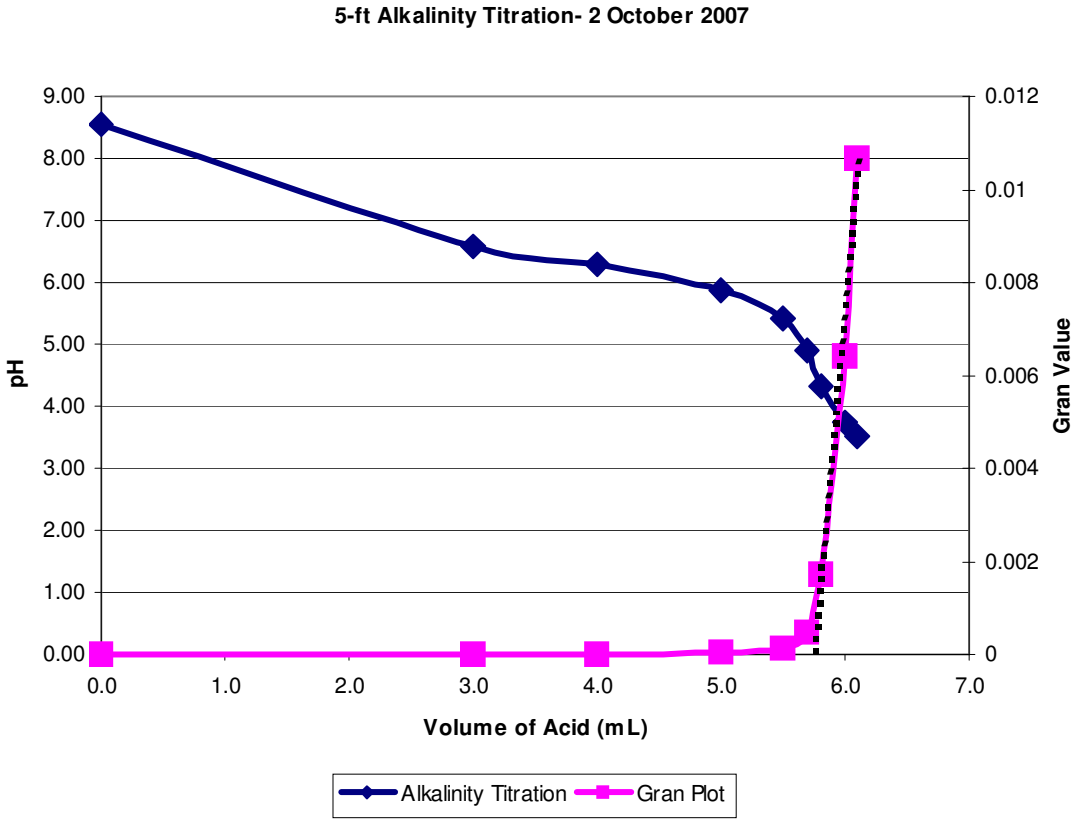

Surface Alkalinity Titration- 24 August 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

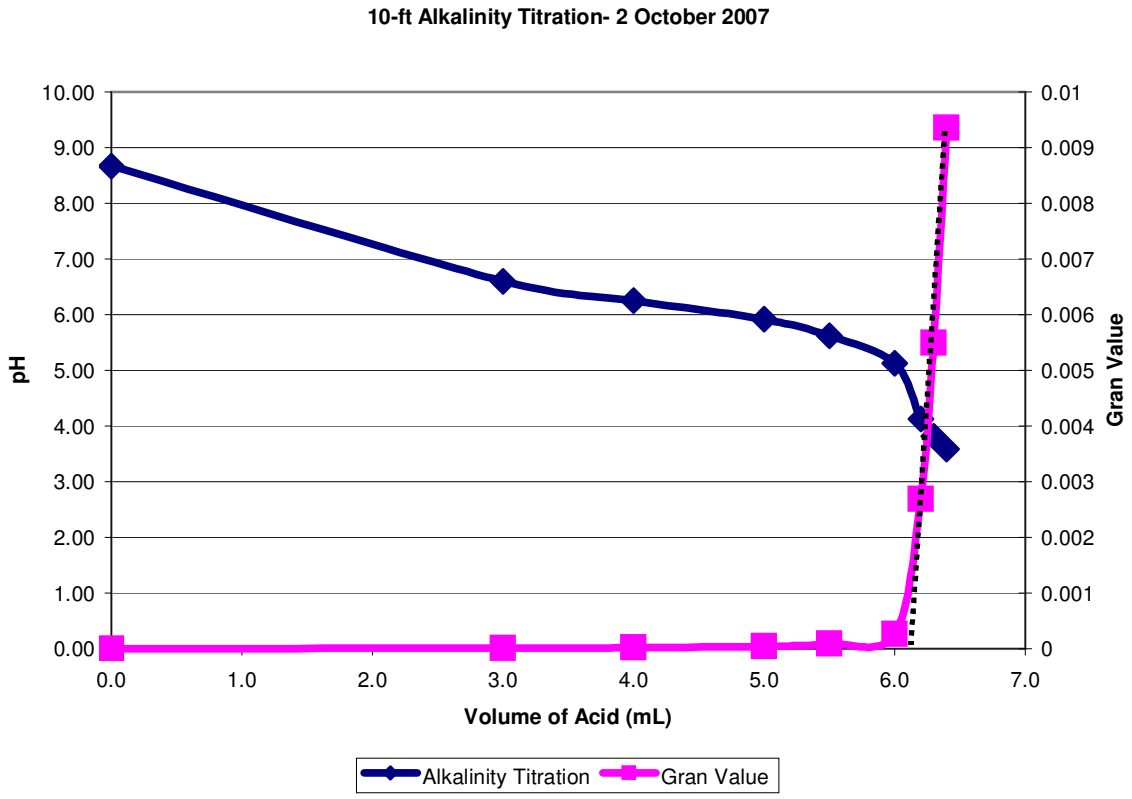

5-m Alkalinity Titration- 24 August 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)

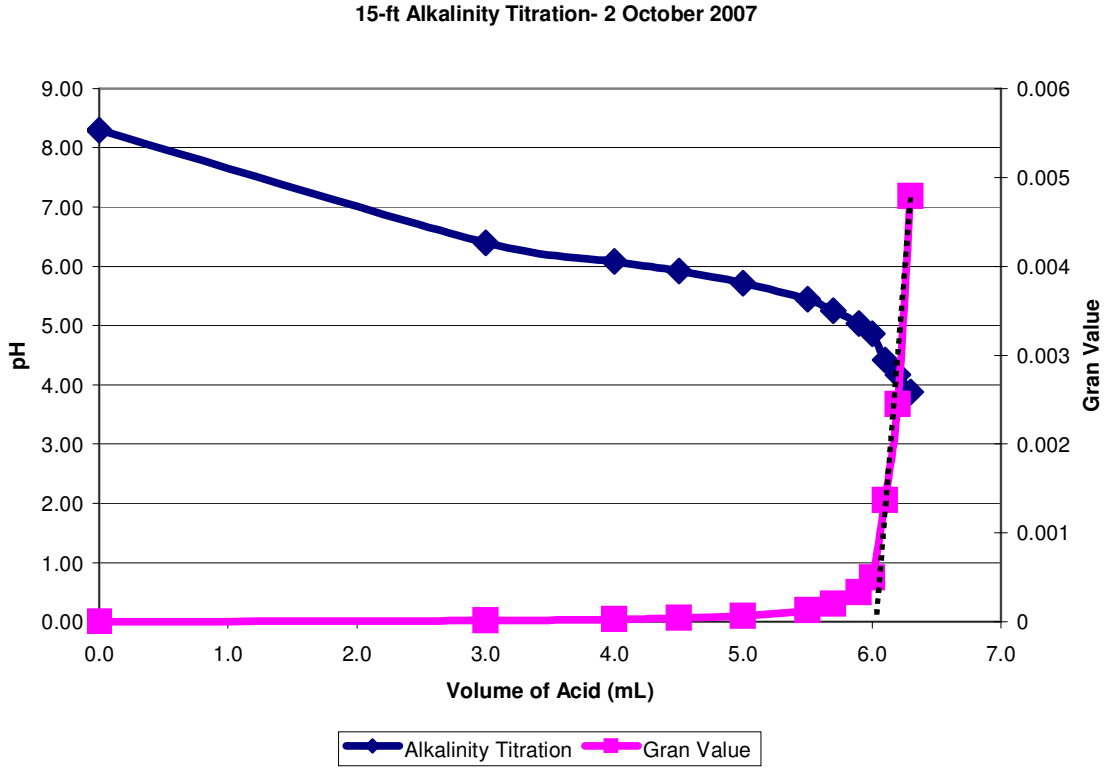

10-m Alkalinity Titration- 24 August 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

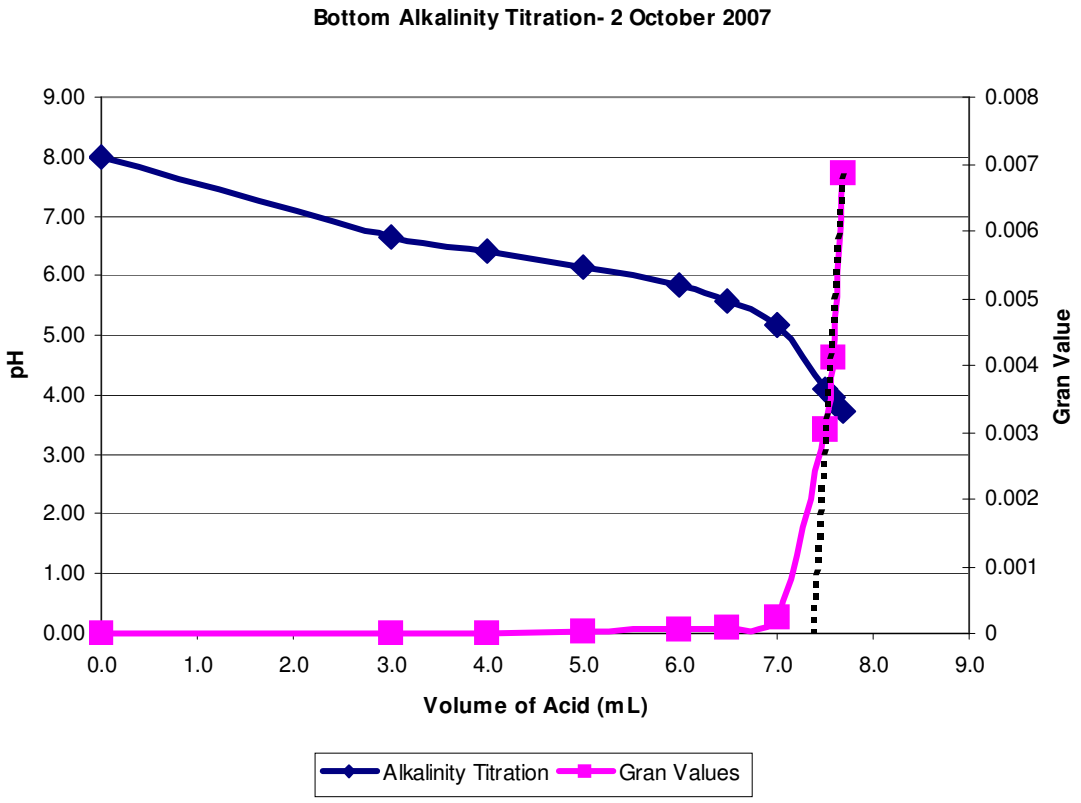

Bottom Alkalinity Titration- 24 August 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

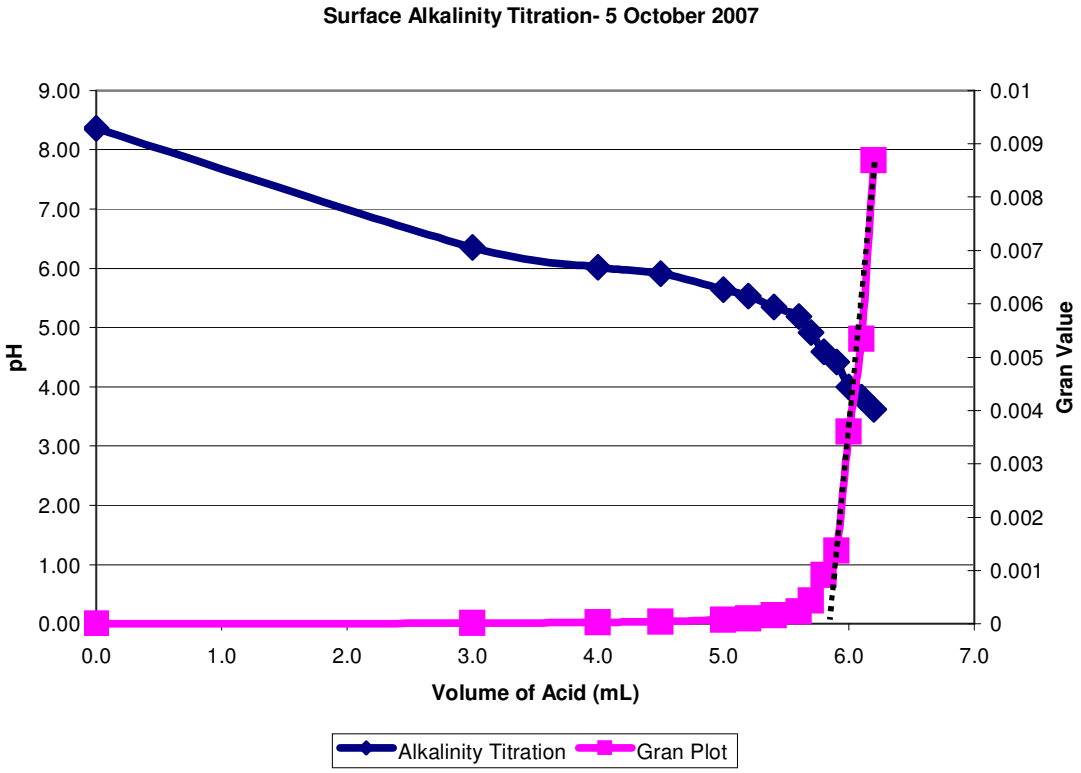

Surface Alkalinity Titration- 2 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

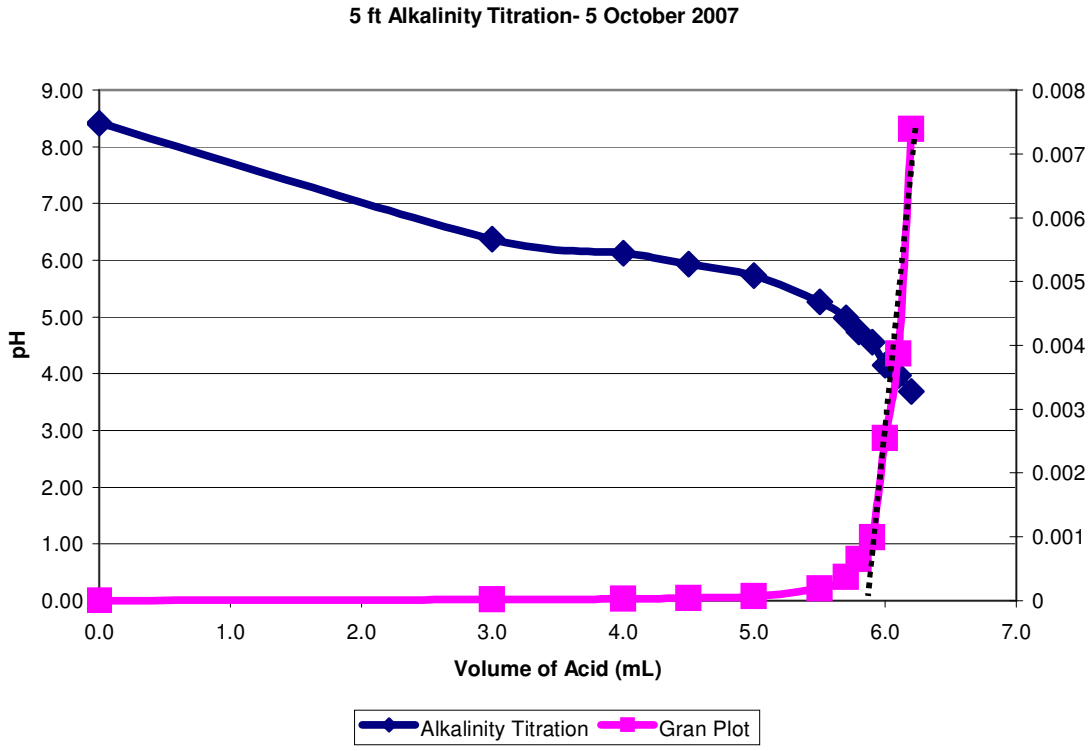

5-ft Alkalinity Titration- 2 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.012
0.01
0.008
0.006
0.004
0.002
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

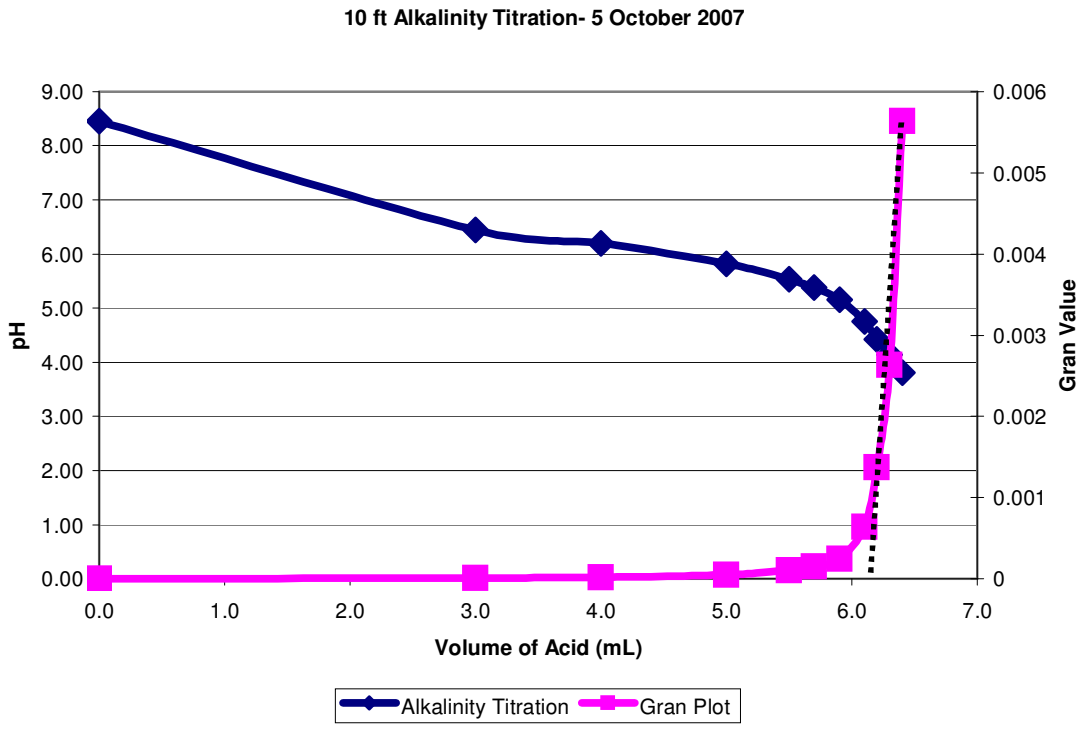

10-ft Alkalinity Titration- 2 October 2007
pH
Gran Value
Volume of Acid (mL)
Alkalinity Titration
Gran Value

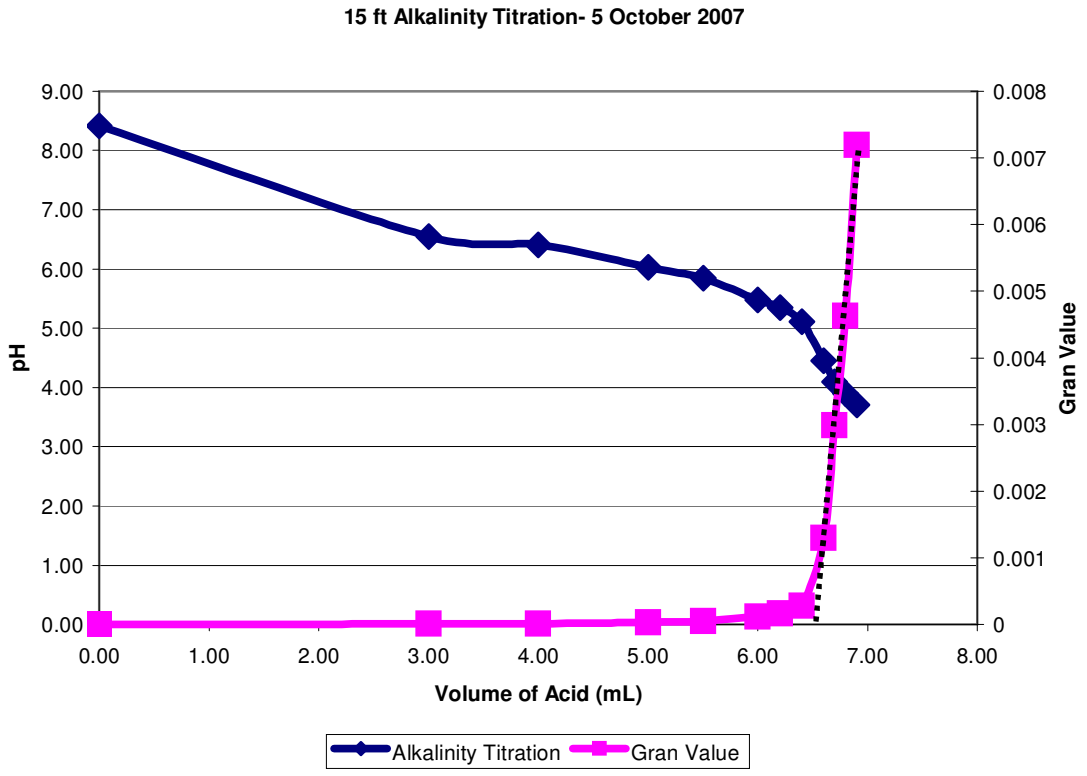

15-ft Alkalinity Titration- 2 October 2007
pH
Gran Value
Volume of Acid (mL)
Alkalinity Titration
Gran Value

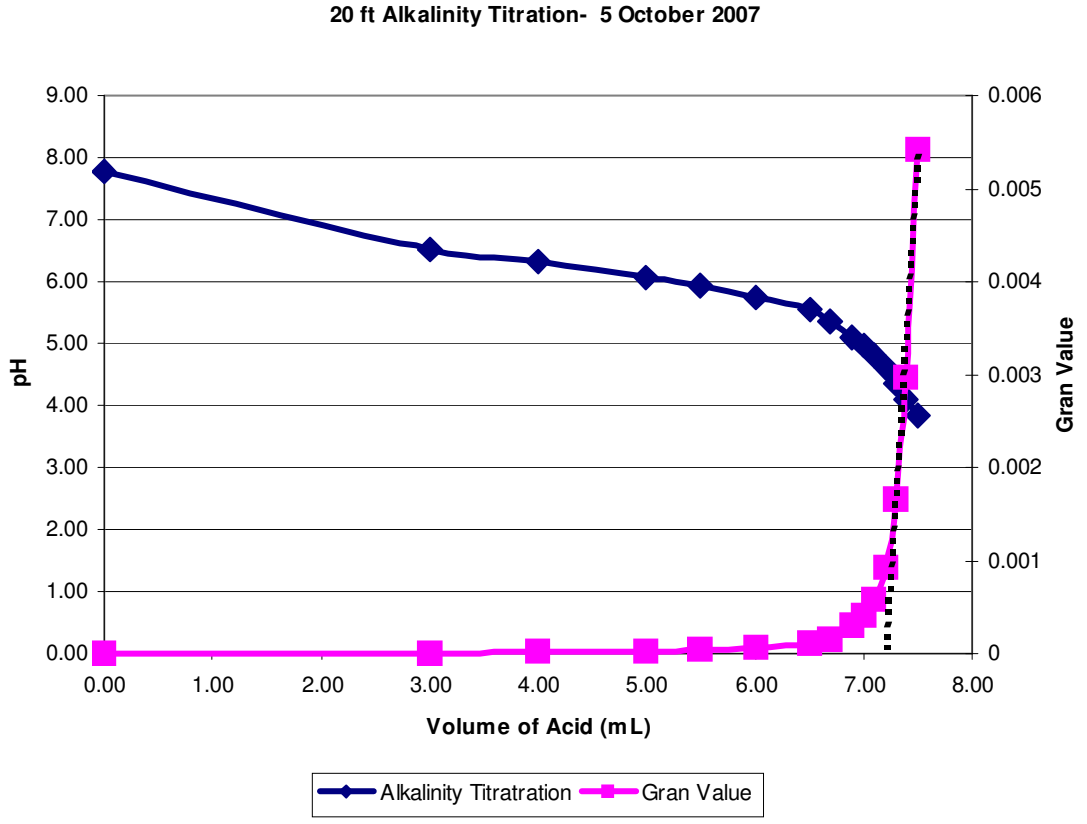

Bottom Alkalinity Titration- 2 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Volume of Acid (mL)
Alkalinity Titration
Gran Values

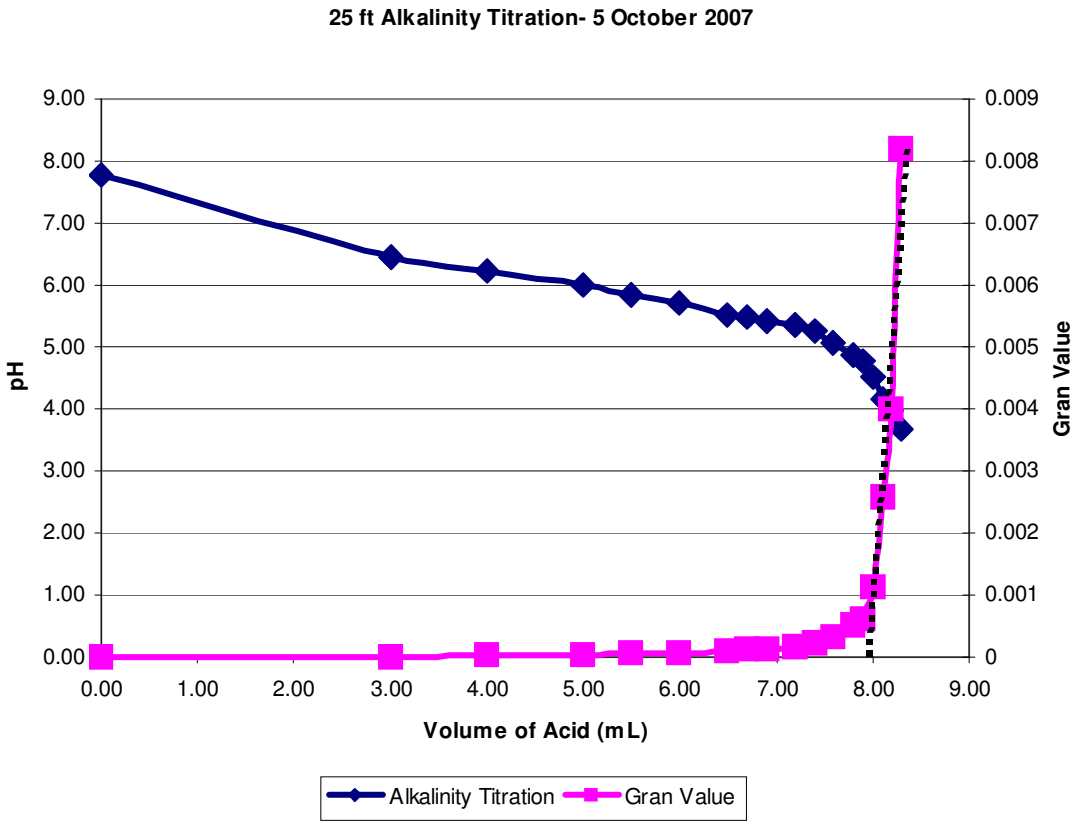

Surface Alkalinity Titration- 5 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

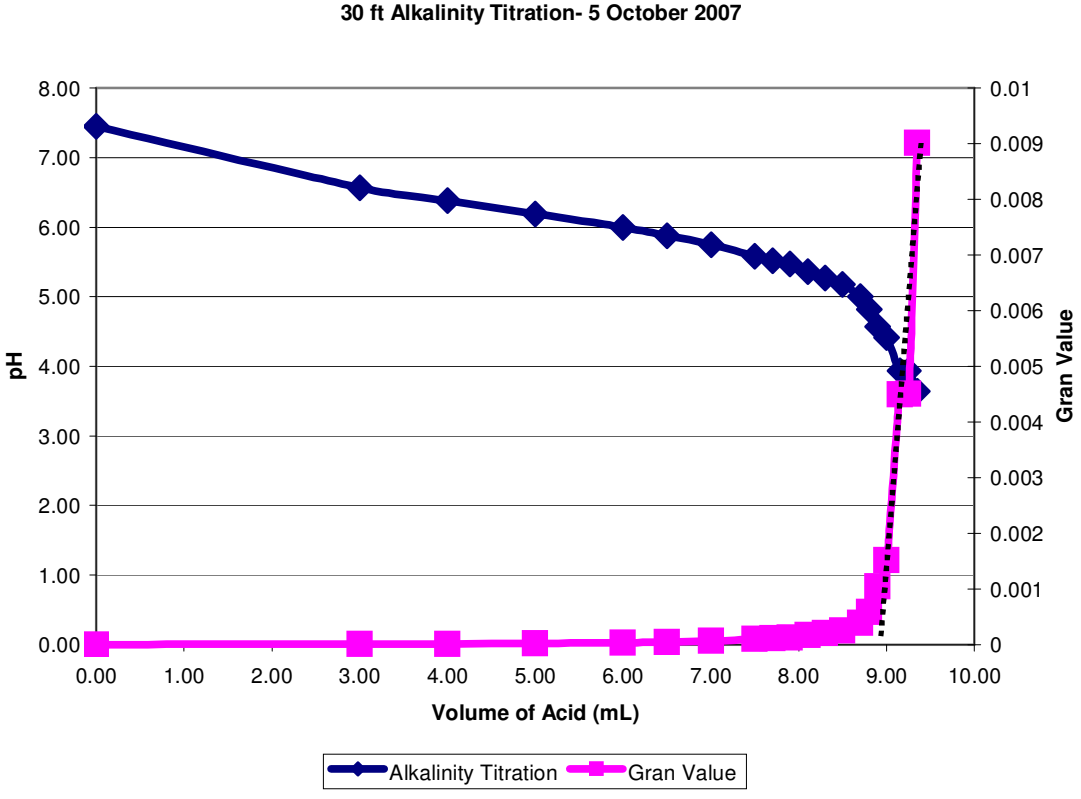

5 ft Alkalinity Titration- 5 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

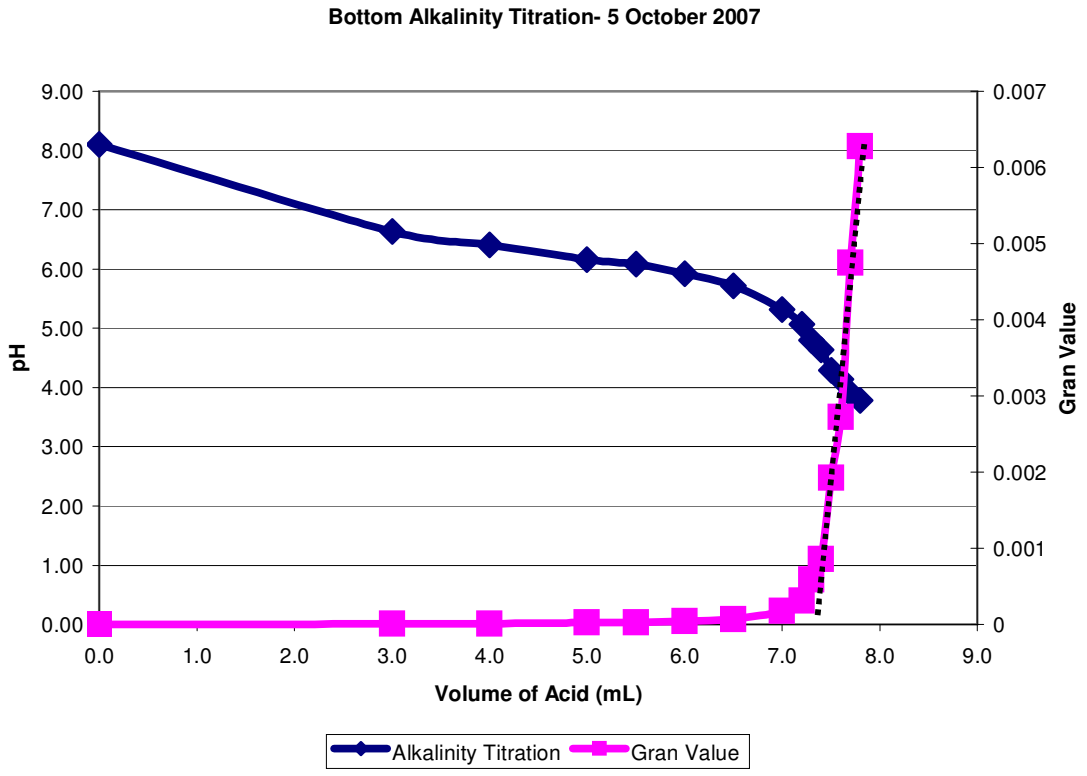

10 ft Alkalinity Titration- 5 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

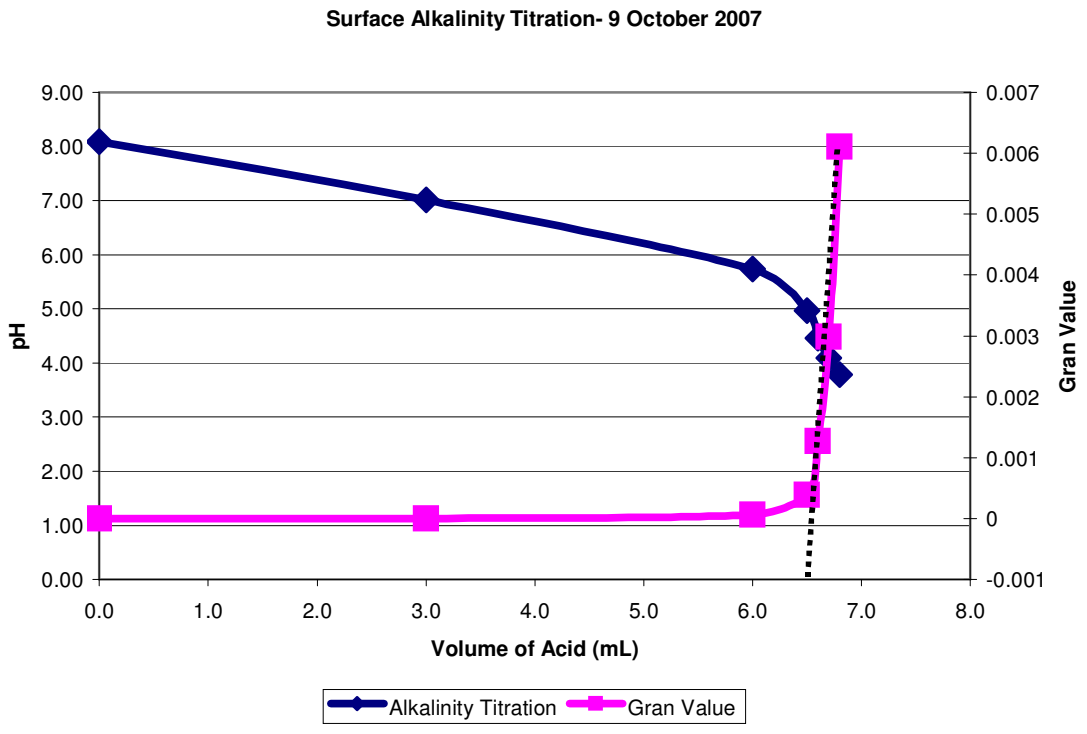

15 ft Alkalinity Titration- 5 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
Volume of Acid (mL)
Alkalinity Titration
Gran Value

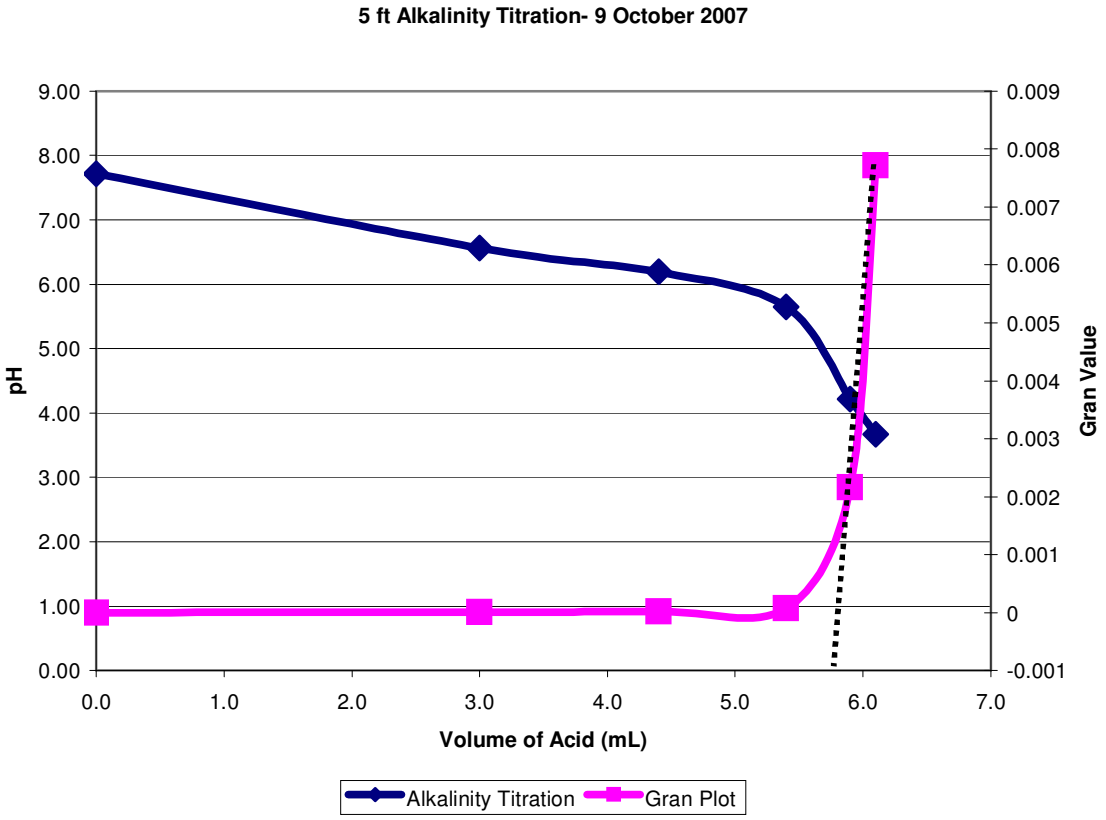

20 ft Alkalinity Titration- 5 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
Volume of Acid (mL)
Alkalinity Titratration
Gran Value

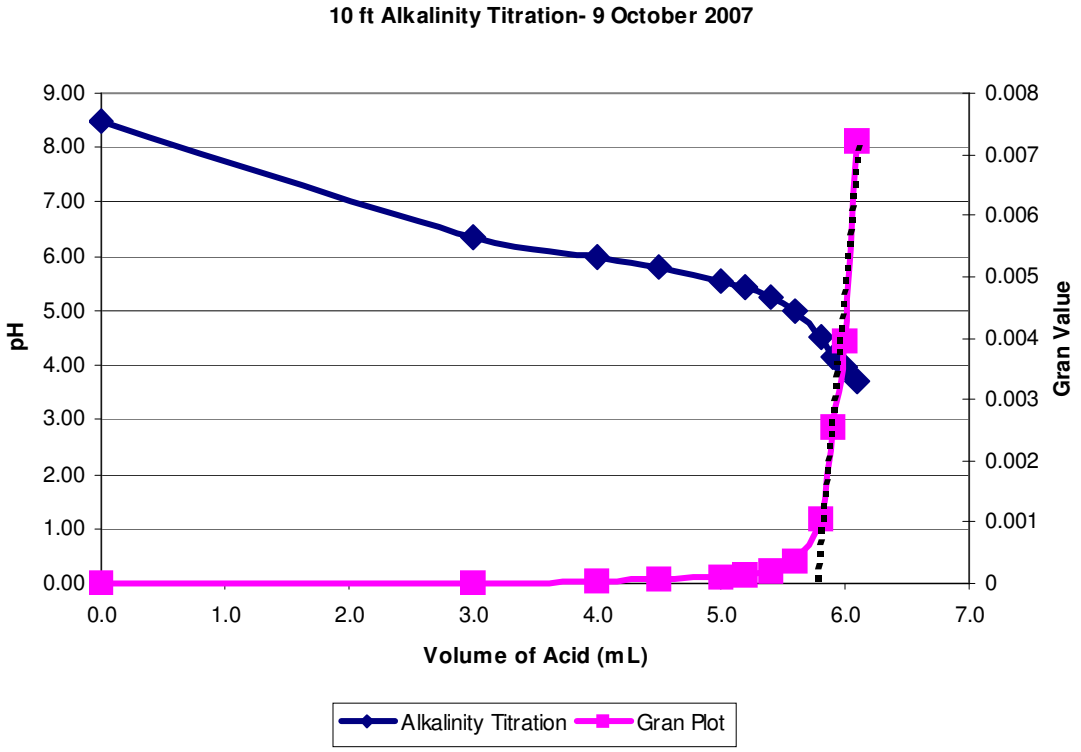

25 ft Alkalinity Titration- 5 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00
Volume of Acid (mL)
Alkalinity Titration
Gran Value

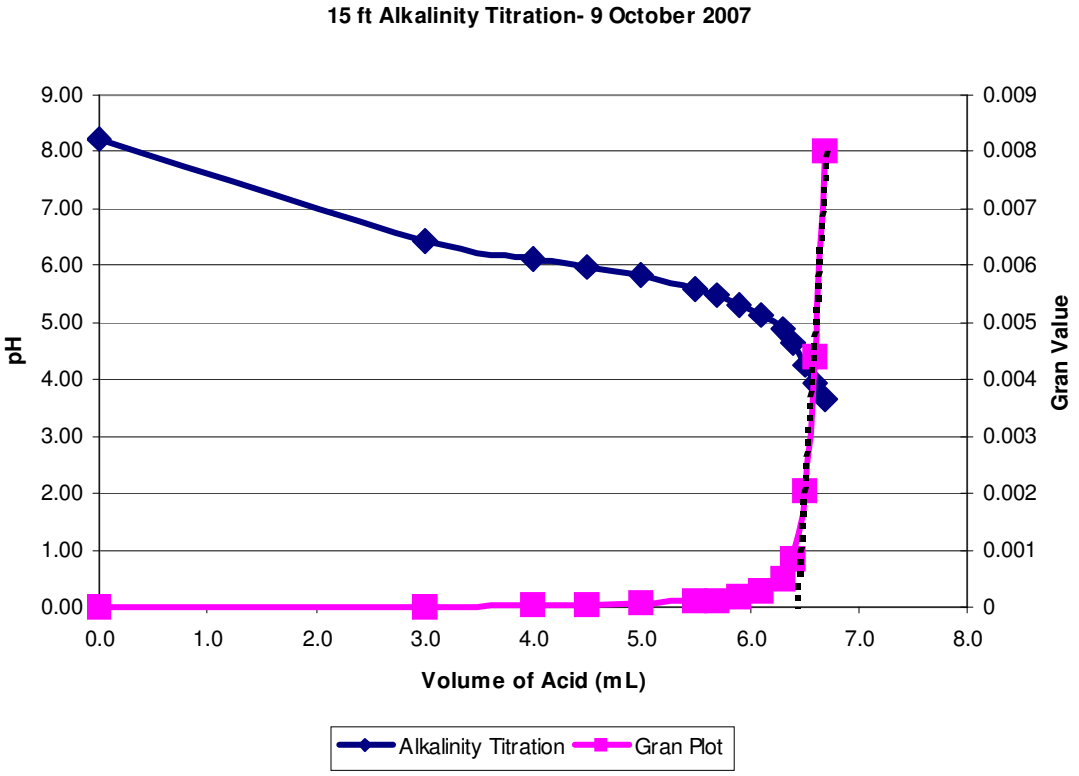

30 ft Alkalinity Titration- 5 October 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00
Volume of Acid (mL)
Alkalinity Titration
Gran Value

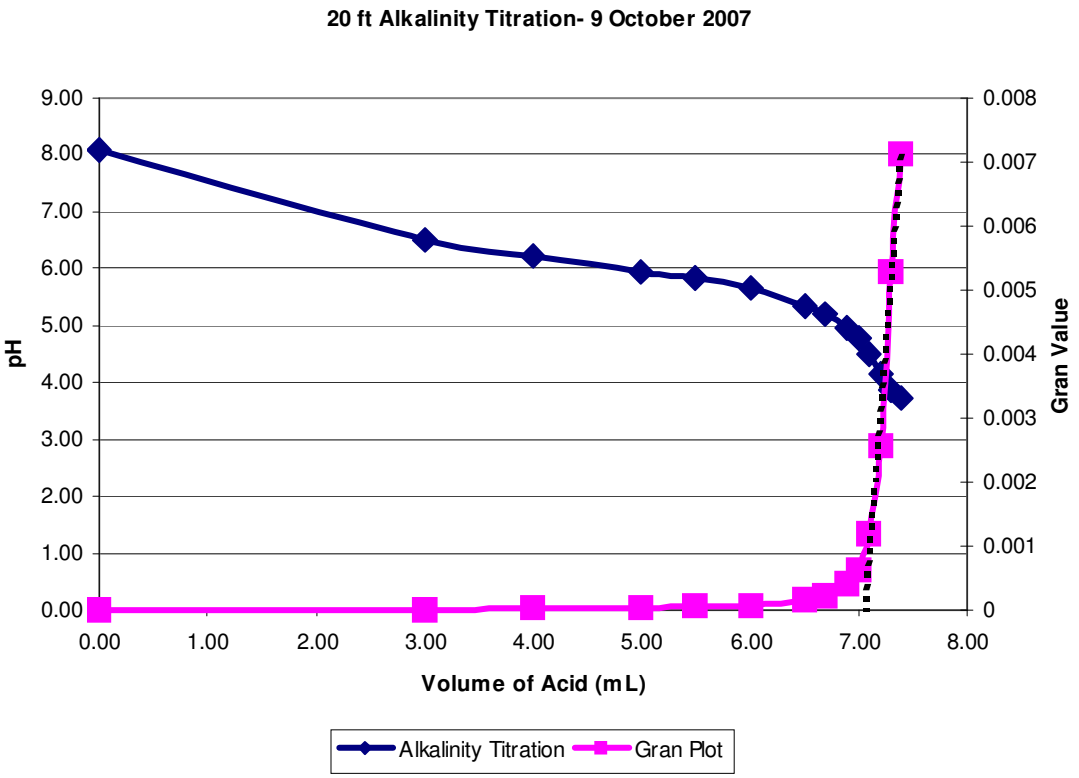

Bottom Alkalinity Titration- 5 October 2007
pH
Gran Value
Volume of Acid (mL)
Alkalinity Titration
Gran Value

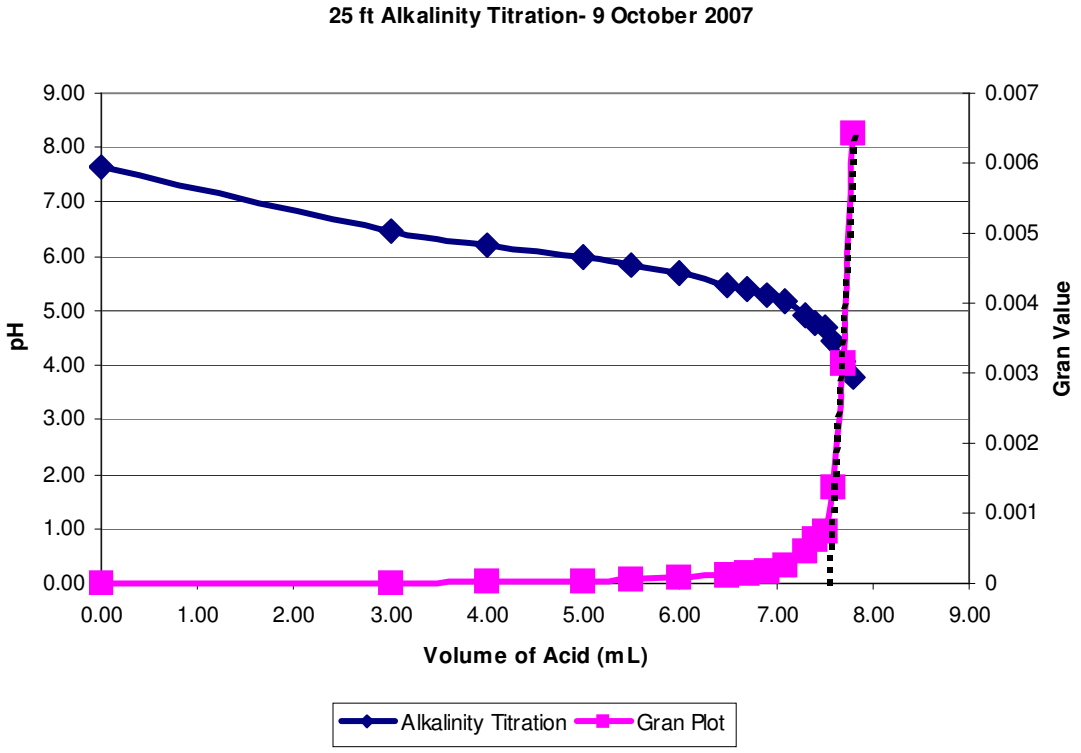

Surface Alkalinity Titration- 9 October 2007
pH
Gran Value
Volume of Acid (mL)
Alkalinity Titration
Gran Value

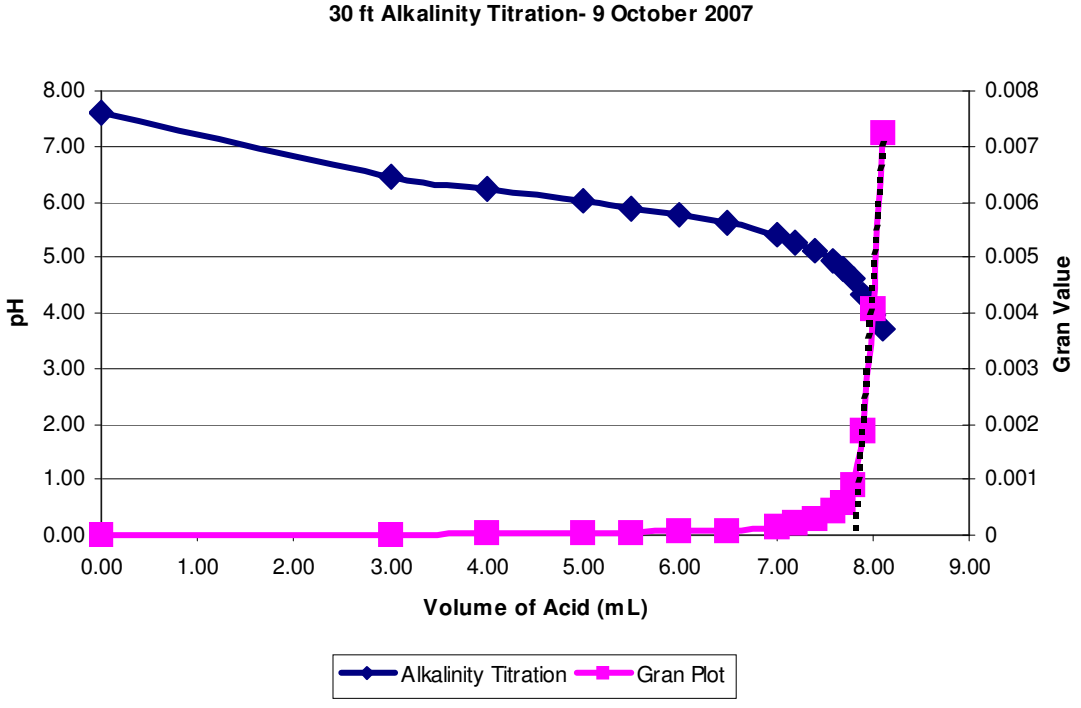

5 ft Alkalinity Titration- 9 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
-0.001
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

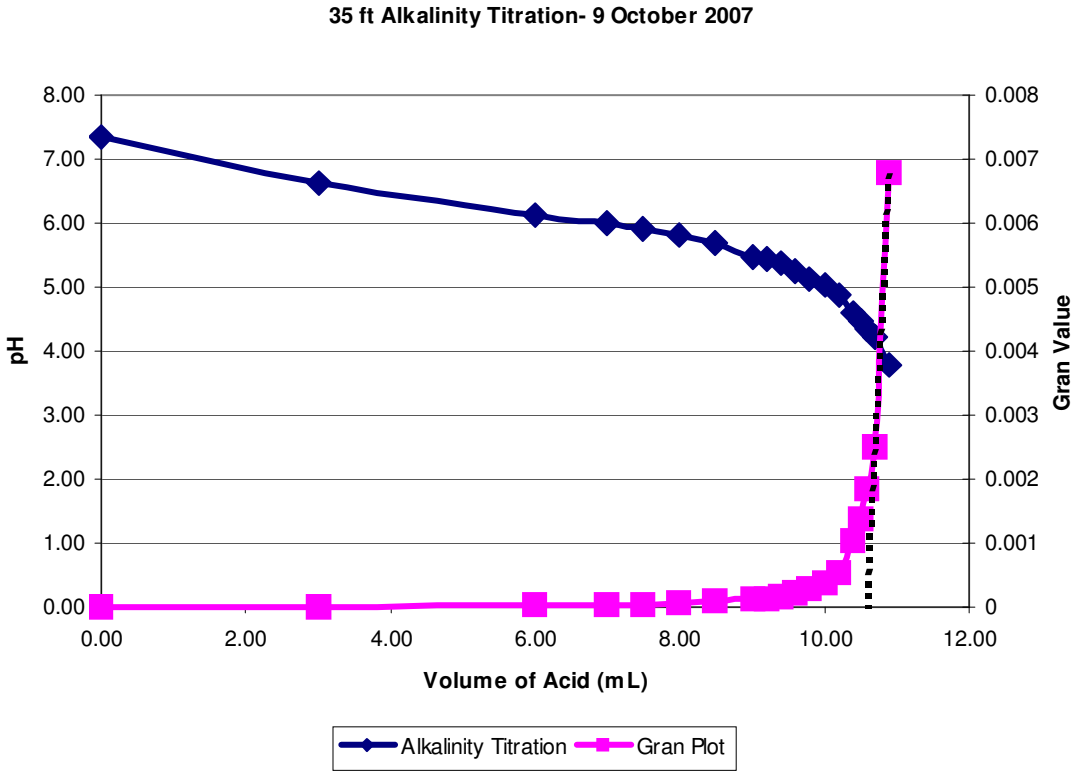

10 ft Alkalinity Titration- 9 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot

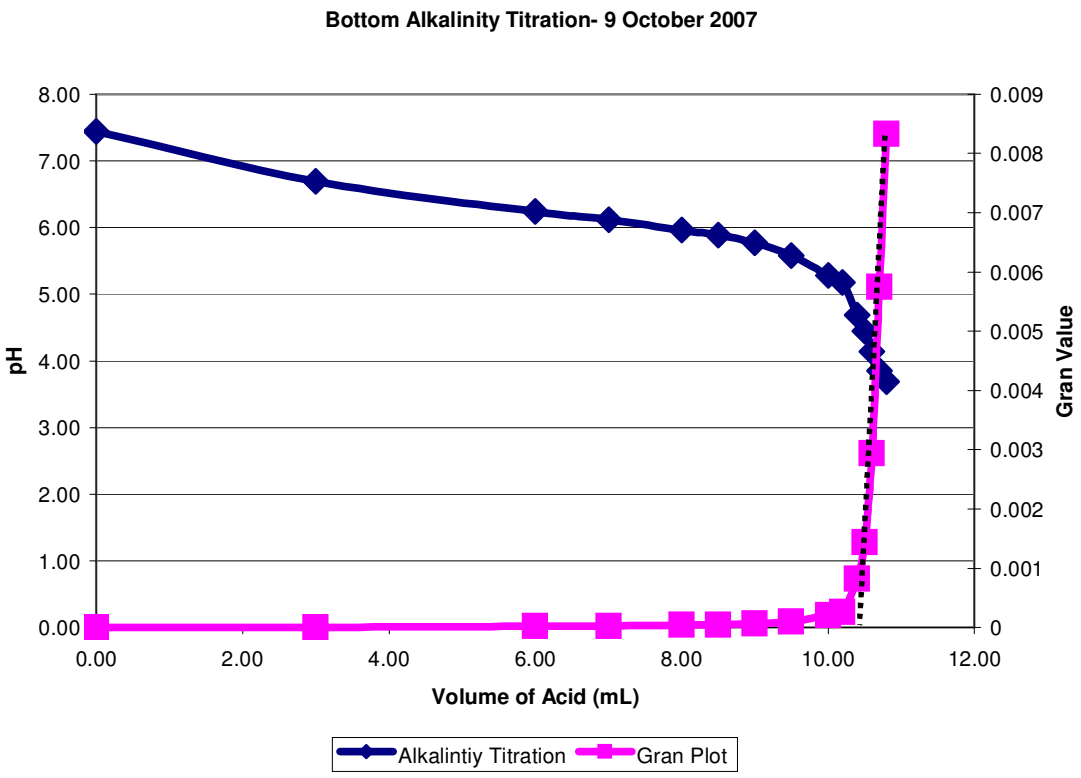

15 ft Alkalinity Titration- 9 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Volume of Acid (mL)
Alkalinity Titration
Gran Plot


20 ft Alkalinity Titration- 9 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
Volume of Acid (mL)
Alkalinity Titration
Gran Plot


25 ft Alkalinity Titration- 9 October 2007
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
Volume of Acid (mL)
Alkalinity Titration
Gran Plot


30 ft Alkalinity Titration- 9 October 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
Volume of Acid (mL)
Alkalinity Titration
Gran Plot


35 ft Alkalinity Titration- 9 October 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.00
2.00
4.00
6.00
8.00
10.00
12.00
Volume of Acid (mL)
Alkalinity Titration
Gran Plot


Bottom Alkalinity Titration- 9 October 2007
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pH
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Gran Value
0.00
2.00
4.00
6.00
8.00
10.00
12.00
Volume of Acid (mL)
Alkalintiy Titration
Gran Plot

E. Carbon Isotope Analysis

17-May	
Depth (m)	**δ13C ‰ V-PDB**
0.2	-8.4
1.6	-8.1
3.1	-7.4
4.6	-6.0
6.1	-9.9
7.7	-10.4
9.1	-10.5
10.7	-11.5
11.0	-11.2

17-Jul	
Depth (m)	**δ13C ‰ V-PDB**
0.2	-6.9
1.6	-7.6
3.1	-7.1
4.6	-7.2
6.1	-10.0
7.7	-10.8
9.2	-10.4
9.9	-10.4

9-Oct	
Depth (m)	**δ13C ‰ V-PDB**
0.3	-5.7
1.5	-4.7
3.1	-5.0
4.6	-8.4
6.1	-10.6
7.6	-11.3
9.2	-12.0
10.7	-10.1
11.5	-9.8
Std. Dev.	0.09